www.ptcer.pl/mccm

MATERIAŁY CERAMICZNE /CERAMIC MATERIALS/, 62, 4, (2010), 456-460

Deposition of PZT on Copper-coated Polymer Films

Gunnar Suchaneck[1]*, Oleg Volkonskiy[1], Gerald Gerlach[1], Zdenek Hubička[2], Alexandr Dejneka[2], Lubomir Jastrabik[2], Steffen Günther[3], Eberhard Schultheiss[3]

[1] TU Dresden, Solid State Electronics Lab, Dresden, Germany
[2] Institute of Physics, Dept. of Optics, Academy of Science of the Czech Republic, Prague, Czech Republic
[3] Fraunhofer Institute for Electron Beam and Plasma Technology, Dresden, Germany
*e-mail: Gunnar.Suchaneck@tudresden.de

Abstract

In this work we analyze the deposition process of (111)-textured $Pb(Zr,Ti)O_3$ (PZT) thin perovskite films directly on copper-coated polymer films. Cu thin films with a thickness of about 200 nm were deposited by DC sputtering in a reel-to-reel processing system onto Kapton® HN films with a thickness of 25 μm comprising an *in-situ* reactively sputtered dielectric TiO_{2-x} adhesion layer. PZT thin films with a thickness of 200 to 400 nm were deposited using a pulse-modulated RF plasma jet system consisting of a hollow cathode for reactive sputtering.

Keywords: PZT thin films, Plasma jet, Deposition, Reactive sputtering

OSADZANIE PZT NA POWŁOKACH POLIMEROWYCH POKRYTYCH MIEDZIĄ

W pracy analizujemy proces osadzania cienkiej powłoki perowskitowej, złożonej z $Pb(Zr,Ti)O_3$ (PZT) o teksturze (111), bezpośrednio na powłokach polimerowych pokrytych miedzią. Cienkie powłoki Cu o grubości około 200 nm zostały osadzone za pomocą stałoprądowego rozpylania jonowego, w układzie przetwarzania szpula na szpulę, na powłoki Kapton® HN o grubości 25 μm, zawierające in-situ reakcyjnie rozpyloną adhezyjną warstwę dielektryczną TiO_{2-x}. Cienkie powłoki PZT o grubości od 200 do 400 nm osadzano przy pomocy układu z palnikiem plazmowym modulowanym impulsowo z częstotliwością radiową (RF), zawierającego katodę wnękową, przeznaczoną do rozpylania reakcyjnego.

Słowa kluczowe: powłoka PZT, palnik plazmowy, osadzanie, rozpylanie reakcyjne

1. Introduction

The deposition of complex oxides on base metal substrates and polymer films represents an important extension of thin-film technology to substrate materials, more compatible with innovative applications. Electronic devices which are directly integrated into printed wiring boards or multi-chip module-laminated structures allow the fabrication of much thinner and sleeker electronics. They decrease manufacturing costs, increase electrical performance, and enhance design flexibility. Alone, the progressive miniaturization of cellular phones creates a huge market for miniaturized passive components. When using perovskite oxide films, additional piezoelectric and pyroelectric functionality is added to embedded components. Flexible polymer substrates also create new application capabilities for sensors and actuators. On the other hand, polymer substrates are incompatible with typical processing temperatures of conventional silicon-based electronics.

The thin film microstructure and resultant film properties are determined by deposition parameters, such as substrate temperature, energy of incident ions, ion and neutral fluxes, deposition rate etc. The ion assisted film deposition is known to increase the surface diffusion of the condensing species [1]. This enables, for instance, the growth of single crystal films on (111) *p*-type silicon substrates at room temperature when the silicon ion current density, which was about 25 % of the total incident silicon atoms, exceeds 80 μA/cm^2 [2]. Previously, it has been demonstrated that increasing the ion to neutral flux ratio J_i/J_n at relatively low nitrogen ion energies of 20 eV results in a similar microstructure of reactively sputtered TiN thin films, as when the substrate temperature is increased [3]. Anatase TiO_2 films were deposited by means of inductively coupled plasmas applied to conventional DC magnetron sputtering (ICP-MS) at a substrate temperature of 160°C while with magnetron sputtering only amorphous films were obtained [4].

Quite an efficient way of generating homogeneous radio frequency (RF) plasmas is constitued the hollow cathode discharge. Here, the electrons oscillate in the hollow cathode, giving rise to a high plasma density [5]. Plasma densities exceeding 10^{14} cm^{-3} were obtained at discharge currents

of 10–25 A in a 1.5-cm-diameter flowing xenon gas hollow cathode [6]. Such plasma density values are about one order of magnitude higher than what can be obtained in a regular magnetron discharge. The on-axis plasma potential inside the cathode was found to be in the 10–20 V range with electron temperatures of 2–5 eV depending on the discharge current and gas flow rate. In a plasma jet the reactive sputtering occurs through an interaction with the material of the nozzle. The plasma expands in a plasma jet through a nozzle into the reactor chamber. Thus, the composition of the nozzle material is transferred to the substrate surface. Low pressure RF plasma jets generate a non-equilibrium plasma with electron temperatures of about 22,000 K, molecules, vibrationally excited up to about 5,000 K, and a gas temperature of about 500 K [7]. In our deposition set-up, the electron density of the RF modulated hollow cathode plasma jet system was determined to be 3×10^{10} cm^{-3} in the jet during the active part of the modulation pulse independent on average power applied to the nozzle [8]. The non-thermal excitation of the species allows perovskite PZT synthesis without sufficient heating of polymer substrates coated with a sputtered (111) Pt bottom electrode [9].

In this work, we analyze the deposition process of PZT thin films on copper-coated polymer films comprising a titania seed layer.

2. Experimental

Copper thin films were deposited inside a reel-to-reel vacuum coating system (Fig. 1) onto 25 μm thick polyimide substrate (DuPont Kapton® HN 100). The 220 mm wide substrate was coated *in-situ* with an titanium dioxide adhesion enhancement layer [10]. The adhesion layer was made by reactive sputtering in oxide mode at sputtering power of 1 kW using a dual magnetron sputtering system. The copper layer was deposited by DC sputtering using a single magnetron at 3 kW sputtering power. All magnetron targets had an area of 350 mm × 120 mm. Both layers were made within one coating run at a web speed of 0.8 m/min. Further preparation details were already reported elsewhere [11].

In order to reduce the interaction of PZT and Cu during the initial growth stage, ultra-thin (less than 10 nm in thickness) amorphous TiO_{2-x} seeding layers with controlled stoichiometry were deposited by reactive sputtering at a substrate temperature of 75°C, corresponding to the start of diffusion-controlled Cu oxidation. Seed layer stoichiometry control was performed by an *in-situ* measurement of the intensity of a spectral Ti line which enables the monitoring of the Ti oxidation degree in the film [12]. The LS703S pulse magnetron sputter system (Von Ardenne Anlagentechnik, Dresden) employed for this purpose (Fig. 2) was described in [13]. Deposition of (111)-textured PZT was performed onto Kapton® HN films coated with both the seed layer and copper using a single RF plasma jet (Fig. 3), following the procedure given in [9]. A stoichiometric PZT cylindrical nozzle acts as the RF hollow cathode which is reactively sputtered. The internal diameter and length of the PZT nozzle were 3 mm and 30 mm, respectively. An intensive hollow cathode discharge was generated inside the PZT nozzle by the pulse modulated RF mode and the plasma jet was created by argon and oxygen flows through the nozzle. The

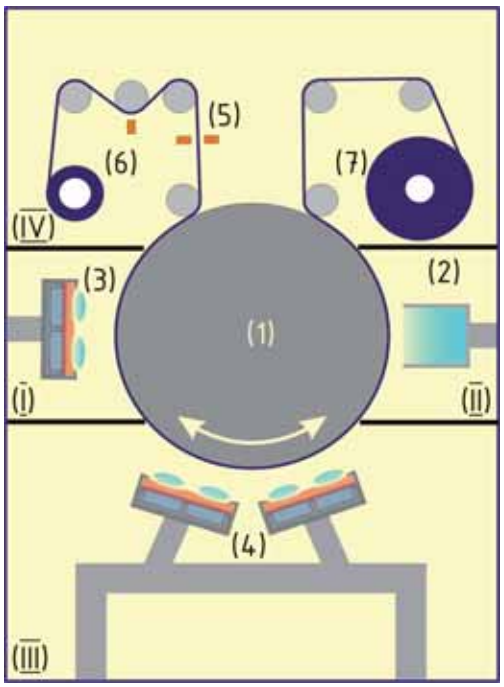

Fig. 1. Reel-to-reel coating system for polymer films. (1) chill roll; (2) pretreating station; (3) Cu magnetron; (4) dual magnetron system for adhesion layer fabrication; (5) sensors of optical transmission; (6), (7) winding rolls; (I)-(III) deposition chambers; (IV) winding chamber.

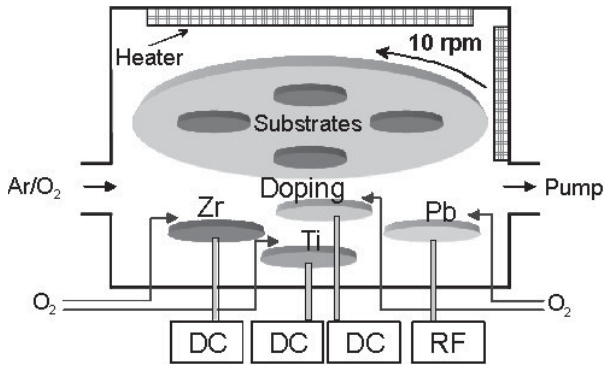

Fig. 2. LS730S multi-target-sputter-deposition facility.

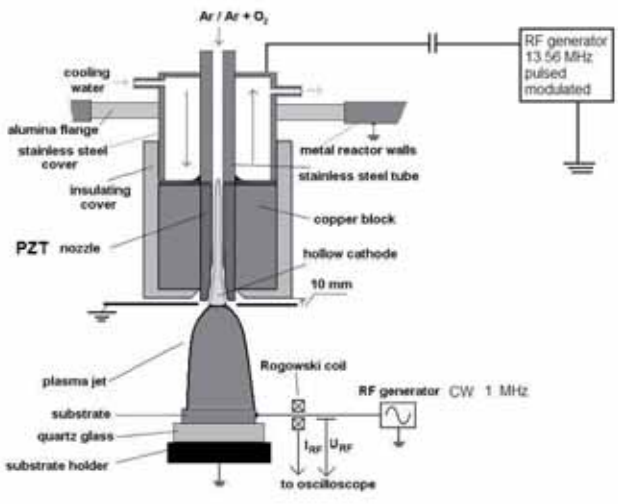

Fig. 3. Experimental setup for PZT plasma jet deposition.

substrate was placed perpendicularly to the plasma jet axis in a distance of 10–40 mm from the hollow cathode outlet. Film stoichiometry was varied by applying a substrate bias and by changing the distance *l* between the PZT nozzle outlet and the substrate [14].

The structure analysis of the deposited films was performed by XRD diffraction. Surface topography and piezoelectric response (both in plane and out of plane) were evaluated by scanning force microscopy. The chemical composition was measured by an electron microprobe JOEL JXA 733. Optical measurements were made by means of a J.A. Woollam spectral ellipsometer, operating in the rotating analyzer mode. The ellipsometric parameters were measured in the spectral range from 300 to 1000 nm at three angles of incidence. The ellipsometric data were analyzed with the software package WVASE32. Optical constants were calculated for a simple substrate/film model taking into account surface roughness and thickness non-uniformity. The complex dielectric behaviour was investigated by means of a Solartron 1260 impedance analyzer. Ferroelectric loops were recorded by a compensated Sawyer-Tower circuit.

3. Results and discussion

The plasma jet film deposition allows a synthesis of perovskite nanoclusters to occur already in the gas phase and a subsequent deposition of a thin film onto the cold substrate surface. This is illustrated by the appearance of (111) textured PZT in a film deposited at an RF power of 400 W, Ar and O_2 flows of 50 and 64 sccm, respectively, a total pressure in the chamber of 6 Pa and a nozzle outlet-substrate distance of 10 mm onto a biased substrate in Fig. 4. A continuous film was formed with an AFM surface roughness of about 40 nm. This relatively high surface roughness is attributed to a low surface mobility of condensable species. However, the film is still a multiphase mixture of different oxides and exhibits a high lead deficiency (Pb/(Zr+Ti) ≈ 0.35) caused by lead resputtering from the surface bombarded by argon ions [15]. On the other hand, ion bombardment favors the formation of the desired perovskite structure.

If the substrate bias is reduced, the lead deficiency decreases and changes to the lead excess of Pb/(Zr+Ti) ≈ 1.05 for an unbiased substrate. This is accompanied by the formation of an increasing amount of the non-ferroelectric pyrochlore structure. The low sticking probability of the volatile PbO species at the initial stage of deposition onto the metallic substrate surface inhibits the formation of the perovskite phase nuclei. As a result, the incubation time for the nucleation increases and an amorphous interface layer is formed. In order to avoid the lead deficiency and pyrochlore structure formation, the PbO flux should be controlled independently, for instance, by using a composite $Pb(Zr,Ti)O_3$-PbO target or by using a multi-plasma-jet reactor as described in [8] for $Ba_xSr_{1-x}TiO_3$ deposition. Here, a different instant RF power was applied to the $SrTiO_3$ (300 W) and $BaTiO_3$ (700 W) nozzles and the time of the active pulse part on both nozzles was varied independently in order to control their sputter rate and to affect the Ba and Sr atomic concentrations in the films. The ratio of Ba/Sr was then determined by the average power applied to the $SrTiO_3$ and $BaTiO_3$ nozzles. The experiments using a multi-plasma jet reactor for independent control of PbO, ZrO_2 and TiO_2 fluxes during nucleation and film growth are in progress now.

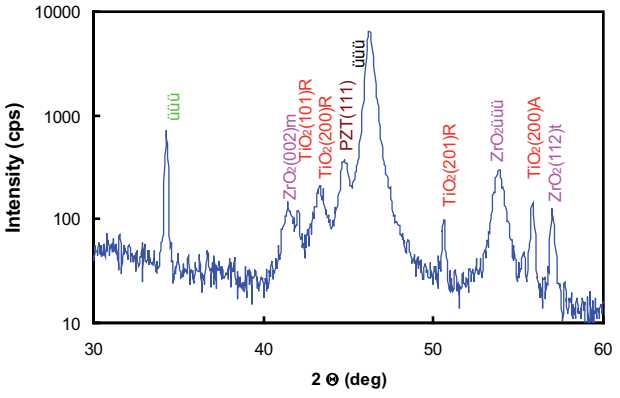

Fig. 4. XRD pattern of a film deposited applying a substrate bias of -70 V and a nozzle outlet-substrate distance of 10 mm.

Fig. 5 shows the spectral dependence of the absorption coefficient in comparison to PZT thin films, deposited by conventional multi-target reactive sputtering and chemical solution deposition [16]. In our case, film opacity in the VIS region is caused not only by the lattice occupation disorder as for reactive sputtered films [16], but additionally also by the multiphase texture of the films. The lower ion bombardment at higher chamber pressures increases the absorption coefficient. This indicates a deterioration of film quality. In result, the ion bombardment during film growth is a key parameter for the improvement of PZT thin films deposited onto copper-coated polymer substrates.

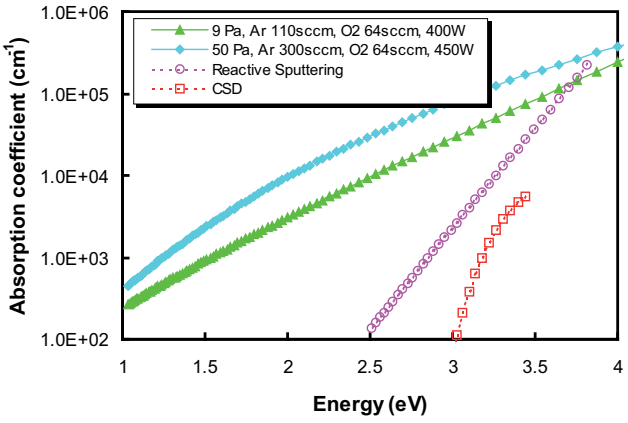

Fig. 5. Spectral dependence of the absorption coefficient of plasma-jet deposited PZT films compared to films deposited by multi-target reactive sputtering and chemical solution deposition [16].

Film stoichiometry was varied by applying a substrate bias and by changing the distance between the PZT nozzle outlet and the substrate. The absence of intentional substrate heating (the substrate is heated solely by bombardment with energetic particles generated in the RF-plasma) is favorable with regard to the large mismatch of the thermal expansion coefficients of sputtered PZT (8.33 ppm/K [17]) and Cu films (~18 ppm/K) [18]). On the other hand, the thermal expansion coefficient of the Kapton® HN substrate (~20 ppm/K) [19]) is well matched to copper. AFM investigations revealed a nearly identical grain size of about 50 nm, both for the Cu and the PZT thin films. This gives evidence that the epitaxial

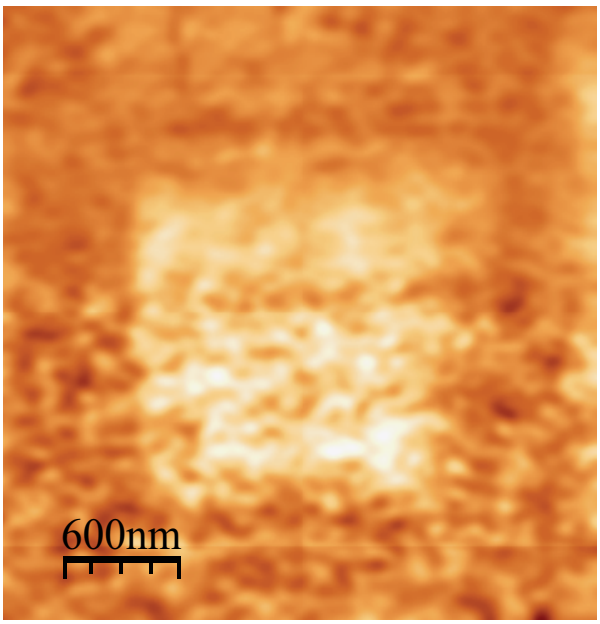

Fig. 6. Piezoelectric image written by the AFM tip. (PZT thin film deposition conditions: RF power 400 W; Ar and O_2 flows 110 and 64 sccm, respectively; total pressure in the chamber 9 Pa, and a nozzle outlet-substrate distance 10 mm).

deposition takes place. The amorphous seeding layer was totally consumed during the initial stage of film deposition. Thus, thermal mismatch between the bottom copper electrode and PZT thin film introduces compressive strain during post-deposition cooling. The mechanically strained interface deforms the underlying foil and the PZT film cracks when the foil is flattened. Consequently, a warpage of the flexible substrate is significantly reduced at low substrate temperatures.

The dielectric constants of optimized samples were in the range 40 to 100, the dielectric losses were 5 to 8 %. Therefore, the films fabricated in this work are competitive with current state-of-the-art materials for embedded capacitors. Since continuous and dense films as thin as 10 nm can be fabricated by our technology, one order of magnitude higher capacitance density may be achieved.

The as-deposited films were self-polarized with polarization pointing to the surface of the sample [20]. Polarization was switchable and a piezoelectric hysteresis was obtained. Polarization switching is illustrated in Fig. 6, demonstrating a piezoelectric image written by the electric field of the AFM tip into a PZT thin film.

The piezoelectric properties of the deposited PZT films could replace ZnO on plastics in flexible pressure sensors [21], piezoelectric dispensers of printing micro-arrays [22], and piezoelectric power generators [23], as well as piezoelectric polymers in tactile imaging arrays [24]. However, it has to be noted that the piezoelectric response of the reported in this work PZT films is still small, about one order of magnitude lower than required for practical application.

4. Conclusions

Kapton® HN films web-coated with a copper thin film electrode in an industrial-scale reel-to-reel system are suitable substrates for PZT thin film deposition. (111)-textured PZT was fabricated on these Cu-coated polymer substrates by means of a RF-modulated plasma–jet system comprising a hollow cathode for reactive sputtering. Film quality may be improved by optimizing the ion bombardment of the growing surface and by an independent control of the lead flux in a multi-jet deposition system. Dielectric properties of the films are suitable for applications such as embedded capacitors. Piezoelectric properties make the films promising to be used in flexible piezoelectric sensors, actuators and power generators.

Acknowledgements

This work was supported by the German Research Council (DFG), Grant GE 779/18, and by the Academy of Science of the Czech Republic, Grants KJB100100703, 202/09/J017 and AV0Z10100522. The authors thank D. Kiselev (Univ. Aveiro) for providing Fig. 6.

References

[1] Müller K.-H.: „Role of incident kinetic energy of adatoms in thin film growth", Surf. Sci., 184, (1987), L375-L382.
[2] Itoh T., Nakamura T., Muromachi M., Sugiyama T.: „Low temperature silicon epitaxy by partially ionized vapor deposition", Jpn. J. Appl. Phys., 16, (1977), 553-557.
[3] Hultman L., Sundgren J.-E., Greene J.E., Bergstrom D.B., Petrov I.: „High-flux low-energy (~20 eV) N^+_2 ion irradiation during TiN deposition by reactive magnetron sputtering: Effects on microstructure and preferred orientation", J. Appl. Phys., 78, (1995), 5395-5403.
[4] Park B., Jung D.-H., Lee G., Lee J.-J., Joo J.-H.: „Synthesis of TiO_2 films by ICP-assisted DC magnetron sputtering", Surf. Coat. Technol., 174-175, (2003), 643-647.
[5] Gewartowski J.W., Watson H.A.: „Principles of electron tubes", Van Nostrand, Princeton (NY), (1956).
[6] Goebel D.M., Jameson K.K., Watkins R.M., Katz, I., Mikellides I.G.: „Hollow cathode theory and experiment I. Plasma characterization using fast miniature scanning probes", J. Appl. Phys., 98, (2005), 113302.
[7] Šicha M., Hubička Z., Soukup. L., Jastrabik L., Čada M., Špatenka P.: „Low pressure RF multi-plasma-jet system for deposition of alloy and composite thin films", Surf. Coat. Technol., 148, (2001), 199-205.
[8] Hubička Z., Virostko P., Tichý M., Čada M., Adámek P., Olejnícek J., Deyneka A., Churpita, O., Valvoda V., Jastrabík L.: „Deposition of $Ba_xSr_{1-x}TiO_3$ thin films by double RF hollow cathode plasma jet system", Contrib. Plasma Phys., 48, (2008), 515 – 520.
[9] Hubička Z., Čada M., Adámek P., Virostko P., Olejníček J., Deyneka A., Jastrabik L., Jurek K., Suchaneck G., Guenther M., Gerlach G., Boháč P.: „Investigation of the RF modulated plasma jet system during the deposition of $Pb(Zr_xTi_{1-x})O_3$ thin films on polymer substrates", Surf. Coat. Technol., 200, (2005), 940-946.
[10] Günther S., Schönberger W., Straach S., Schiller, N., Kirchhoff V.: „Flexible circiut board material and method for producing the same", Patent WO 002008138532 A1, 20.11.2008.
[11] Günther S., Fahland M., Fahlteich J., Schiller N.: „Vacuum web coating technologies for flexible electronics", Proc. Int. Symp. Flex. Electronics & Display (ISFED), Hsinchu, Taiwan (2007).
[12] May C., Milde F., Teschner, G.: „Process development for large area reactive magnetron sputtering", Proc. 45th Annual Technical Conference of the Society of Vacuum Coaters, Lake Buena Vista (FL), USA (2002).
[13] Suchaneck G., Lin W.-M., Vidyarthi V.S., Gerlach G., Hartung, J.: „Perspectives of large area $Pb(Zr.Ti)O_3$ thin film deposition", J. Europ. Ceram. Soc., 27, (2007), 3789-3792.

[14] Suchaneck G., Hubicka Z., Dejneka A., Guenther, M., Günther S., Meyer B., Jastrabik L., Gerlach, G., Schultheiss E.: „Deposition of PZT thin films on copper-coated polymer foils – challenges and perspectives", Ferroelectrics, 379, (2009), 107-112.
[15] Krupanidhi S.B., Hu H., Kumar V.: „Multi-ion reactive sputter deposition of ferroelectric $Pb(Zr,Ti)O_3$ thin films", J. Appl. Phys., 71, (1992), 376-388.
[16] Suchaneck G., Lin W.-M., Gerlach G., Deyneka A., Jastrabik L.: „Multi-target reactive sputter deposition of lead-enriched $Pb(Zr,Ti)O_3$ thin films", Integrated Ferroelectrics, 80, (2006), 189-195.
[17] Bruchhaus R., Pitzer D., Primig R., Schreiter M., Wersing W: „PZT thin films grown by multi-target sputtering: Analysis of thin film stress", Integrated Ferroelectrics, 21, (1998), 461-467.
[18] Kuru Y., Wohlschlögel M., Welzel U., Mittemeijer E.J.: „Crystallite size dependence of the coefficient of thermal expansion of metals", Appl. Phys. Lett., 90, (2007), 243113.
[19] Du Pont Kapton® HN datasheet, URL: http://www.dupont.com.
[20] Suchaneck G., Hubicka Z., Jastrabik L., Dejneka A., Kiselev D., Bdikin I., Kholkin A., Gerlach G.: „Deposition of PZT thin films on copper-coated polymer foils Reliability and Properties of Electronic Devices on Flexible Substrates", edited by J.R. Greer, J. Vlassak, J. Daniel and T. Tsui, Mater. Res. Soc. Symp. Proc., Volume 1116E, (2009), 1116E-I03-05.
[21] Kuoni A., Holzherr R., Boillat M., de Rooij N.F.: „Polyimide membrane with ZnO piezoelectric thin film pressure transducers as a differential pressure liquid flow sensor", J. Micromech. Microeng., 13, (2003), S103-S107.
[22] Kuoni A., Boillat M., de Rooij N.F.: „A highly parallel piezoelectric printing device for micro-array technology", 17th IEEE International Conference on Micro Electro Mechanical Systems (MEMS). IEEE, Piscataway (N.J.), (2007), 466-469.
[23] Gao P.X., Song J., Liu J., Wang Z.L.: „Nanowire piezoelectric nanogenerators on plastic substrates as flexible power sources for nanodevices", Adv. Mat., 19, (2007), 67-72.
[24] Kolesar E.S., Dyson, C.S.: „Object imaging with a piezoelectric robotic tactile sensor", J. Micro-electromech. Syst., 4, (1995), 87-96.

♦

Received 30 March 2010; accepted 5 May 2010