Metrology and Materials Characterization

Mater. Res. Soc. Symp. Proc. Vol. 872 © 2005 Materials Research Society J1.3

Modification of deposition process of piezoelectric polycrystalline film by hydrothermal method -Improvement of the deposition process by pre-treatment using hydrogen peroxide

Akito Endo[1], Norimichi Kawashima[1], Shinichi Takeuchi[1]
Mutsuo Ishikawa[2] and Minoru Kurosawa[2]
[1]Toin University of Yokohama, Department of Biomedical Engineering,
1614 Kurogane-cho, Aoba-ku, Yokohama, Kanagawa, 225-8502, Japan
[2]Tokyo Institute of Technology, 4259 Nagatuta-machi, Midori-ku, Yokohama 226-8503, Japan

ABSTRACT

We have studied on hydro-thermally synthesis of Pb(Ti,Zr)O_3 (PZT)piezoelectric polycrystalline thick film on titanium (Ti) substrate. The purpose of this study is resolving the problems for application of PZT hydrothermal polycrystalline thick film to the ultra miniature high frequency medical ultrasound array probe. The problems were the existence of pinholes in the deposited PZT film, the rough surface of that, low dielectric breakdown electric field etc. The surface of Ti substrate was pretreated to have hydrophilic property by using high reactivity of hydrogen peroxide for resolving the problems in this study. As results, hydrophilic property on the surface of Ti substrate was improved. Surface of PZT hydrothermal polycrystalline thick film without pinholes and smooth surface of that were obtained. Furthermore, the material properties like density, Young's modulus and piezoelectric constant d_{31} were increased by the pretreatment of Ti substrate. Consequently, dielectric breakdown electric field of PZT hydrothermal polycrystalline film was improved.

INTRODUCTION

Recently, we have studied on hydro-thermally synthesis of PZT piezoelectric polycrystalline thick film on titanium (Ti) substrates[1], and developed ultrasound sensors[2],[3] by using the PZT hydrothermal polycrystalline thick film (PZT-HPTF) on Ti substrate. Ohba *et al* had studied actively on deposition of PZT film by hydrothermal method[4]-[6]. However, they did not study on the application for the ultrasound sensor. Deposition of PZT-HPTF has the advantages like needless of sintering process, annealing process, polling process etc[7]. PZT-HPTF can be deposited on the Ti substrate with complex shape or tiny shape. On the other hand, PZT-HPTF has disadvantages like unstable material properties, low piezoelectric constants, rough surface of the film, existence of many pinholes, low dielectric breakdown electric field etc. The purpose of this study is resolving above problems in order to apply PZT-HPTF to the ultra-miniature high frequency medical ultrasound array probe like intra vascular ultrasound probe (IVUS probe). The ultra-miniature high frequency medical ultrasound probe should have many extremely tiny piezoelectric elements. PZT piezoelectric ceramics or polymer piezoelectric films like PVDF were

CAMBRIDGE

Cambridge University Press
978-1-107-40894-4 - Micro- and Nanosystems—Materials and Devices: Materials Research Society Symposium Proceedings: Volume 872
Editors: Cengiz S. Ozkan, David A. LaVan, Mark McNie and Somuri Prasad
Excerpt
More information

employed. There was the problem like low yield rate for production of the ultrasound probe with such tiny piezoelectric elements. We think PZT-HPTF is ideal piezoelectric material except above disadvantage for the high frequency tiny ultrasound probes. Therefore, we tried to resolve the problems in PZT-HPTF by pretreatment of Ti substrate. Chemical cleaning was performed on Ti substrate before deposition in the conventional deposition process of PZT-HPTF. The chemical cleaning is the removing process of impurity or contamination on the Ti substrate. We did not consider the modification of Ti substrate to proper condition for deposition of PZT-HPTF. The surface of Ti substrate with anti-corrosive was pretreated to have hydrophilic property by using high reactivity of hydrogen peroxide in this study. The property of PZT-HPTF was estimated in order to resolve the problems in the hydrothermal synthesizing method of PZT film by using a bimorph vibrator with PZT-HPTF deposited on the Ti substrate with the pretreatment.

EXPERIMENTAL DETAILS

Hydrothermal synthesis of PZT-HPTF

The apparatus for hydrothermal synthesis of PZT-HPTF is shown in Fig. 1. Aqueous solutions with precursor materials including metal ions of Ti^{4+} AZr^{4+} APb^{2+} are mixed with a mineralizer of KOH solution in a Teflon coated tank of the apparatus. The PZT-HPTF can be deposited on the titanium substrates under high temperature and high pressure. The conditions such as concentration and volume of the source materials, synthesizing time, synthesizing temperature etc are shown in Table I. PZT crystal nuclei were deposited on the Ti substrate for synthesizing time of 24 hours and at temperature of 180 °C. This process is called as nucleation Process. The PZT crystal nuclei are usually grown in the crystal growth process. However, only nucleation process was performed and property of deposited PZT-HPTF of crystal nuclei was estimated.

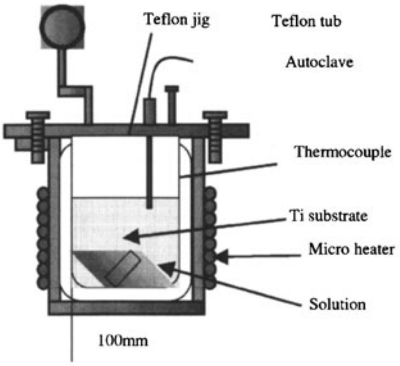


Figure 1. Apparatus for hydrothermal method of PZT piezoelectric polycrystalline film on Ti substrate

CAMBRIDGE

Cambridge University Press
978-1-107-40894-4 - Micro- and Nanosystems—Materials and Devices: Materials Research Society Symposium Proceedings: Volume 872
Editors: Cengiz S. Ozkan, David A. LaVan, Mark McNie and Somuri Prasad
Excerpt
More information

Table I. Quantity and concentration of source materials for hydrothermal synthesizing of PZT films

Nucleation process for 24hours at temperature of 180 °C		
Source material	Concentration	Quantity
$ZrOCl_2$¥$8H_2O$(1N)	0.535mol/*l*	37.5g
TiO_2		1.2g
$Pb(NO_3)_2$	0.520mol/*l*	12.3g
KOH	4N	205.5g

Pretreatment of Ti substrate by using hydrogen peroxide

Ti substrates are pretreated with hydrogen peroxide after chemical cleaning in this study. Methanol, acetone, methanol and distilled water were used one after another as the cleaning liquids in the chemical cleaning process. Ti substrate was washed by ultrasound for 10 minutes in each cleaning liquids. Ti substrate was immersed in the hydrogen peroxide solution with concentration of 30 % for 60 minutes in the pretreatment process. Ti substrates with and without the pretreatment were prepared for consideration of the effect of pretreatment with hydrogen peroxide. PZT-HPTF was deposited on both Ti substrates with same process and same condition except the pretreatment.

RESULTS AND DISCUSSIONS

Effect on Ti substrate

Relationship between the pretreatment time and contact angle was measured by a contact angle meter (CA-X, FACE) for investigation of hydrophilic property on the Ti surfaces with and without the pretreatment by using hydrogen peroxide. It was found as shown in Fig. 2 that the contact angle on the Ti substrate which was immersed in hydrogen peroxide solution tend to decrease with increase of pretreatment time. The contact angle was decreased remarkably and hydrophilic property was increased with increase of pretreatment time from 0 minute to 60 minutes. The contact angle did not change remarkably with pretreatment time for more than 60 minutes. The surface condition of Ti substrate was investigated by an X-ray diffraction meter (XRD; RINT2000, RIGAKU). Figure 3 shows the XRD patterns on the surfaces of Ti substrates with and without pretreatment in the hydrogen peroxide solution for 60 minutes. It was found that the surface of Ti substrate with the pretreatment was degenerated from Ti to TiO_2 or TiO. TiO_2 is stable material. On the other hand, TiO is reactive material. Therefore, TiO is useful for the hydrothermal synthesis of PZT.

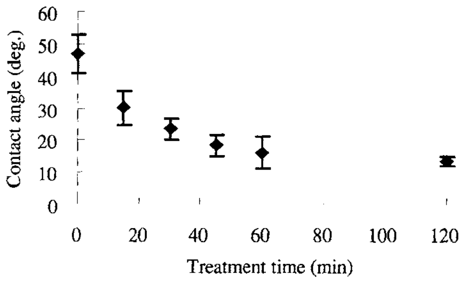


Figure 2. Relationship between pretreatment time in hydrogen peroxide and contact angle on the surface of titanium substrate

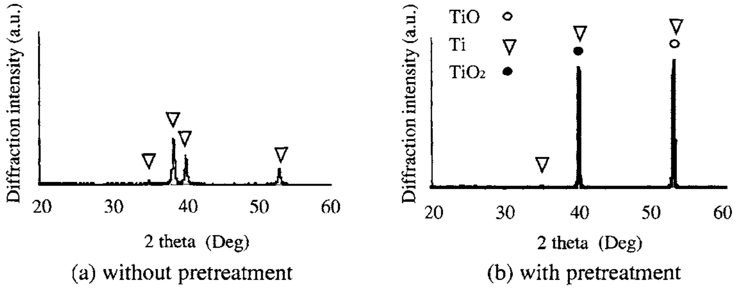


Figure 3. XRD patterns on Ti substrates with and without pretreatment using hydrogen peroxide

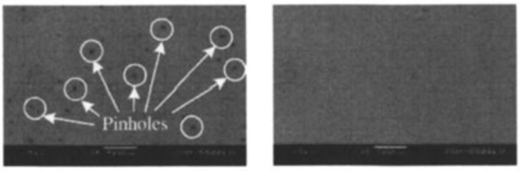
Estimation of deposited PZT polycrystalline film

Figures 4(a) and (b) show the SEM images of PZT-HPTF deposited on the Ti substrate without and with pretreatment by using hydrogen peroxide respectively. We could observe many pinholes on the surface of PZT-HPTF deposited on Ti substrate without pretreatment. On the contrary, pinholes did not exist PZT-HPTF on the substrate with pretreatment. Furthermore, Figures 5(a), (b) show the SEM images of PZT polycrystalline particles deposited on the Ti substrate without and with pretreatment. It was found that larger PZT crystal nuclei could be synthesized on the Ti substrate with pretreatment than that without pretreatment. Figure 6(a) and (b) show the SEM images of cross section of PZT-HPTF on the substrate without and with pretreatment, respectively. Roughness on the surface of PZT-HPTF can be suppressed by pretreatment of Ti substrate.

Furthermore, XRD patterns on the surface of deposited PZT-HPTF were measured. As results, we could observe the XRD patterns showing perovskit structure of PZT regardless of pretreatment of Ti substrate. It was confirmed from the measured results with the Energy dispersive X-ray spectroscopy (EDS) that both deposited PZT films with and without pretreatment had similar chemical compositions.

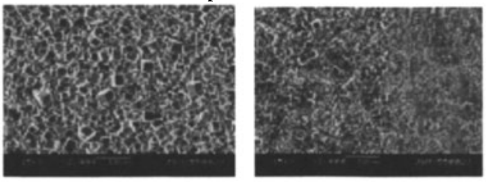
CAMBRIDGE

Cambridge University Press
978-1-107-40894-4 - Micro- and Nanosystems—Materials and Devices: Materials Research Society Symposium Proceedings: Volume 872
Editors: Cengiz S. Ozkan, David A. LaVan, Mark McNie and Somuri Prasad
Excerpt
More information



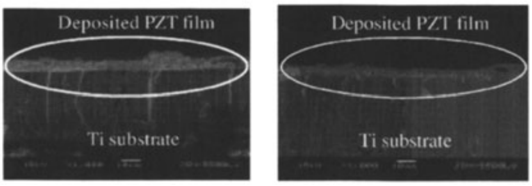
(a) without pretreatment (b) with pretreatment

Figure 4 SEM images on surfaces of PZT polycrystalline films deposited on Ti substrates with and without pretreatment.



(a) without pretreatment (b) with pretreatment

Figure 5 SEM images of PZT poly-crystals deposited on Ti substrates with and without pretreatment.



(a) without pretreatment (b) with pretreatment

Figure 6 SEM images of cross section of PZT polycrystalline films deposited on Ti substrates with and without pretreatment.

Thickness of deposited PZT films and their material properties.

Table II shows the measured results of thickness and the material property of PZT-HPTF deposited on the Ti substrates with and without pretreatment by using hydrogen peroxide. It was found that density, Young's modulus and piezoelectric constant d_{31} were increased by pretreatment of Ti substrate with hydrogen peroxide. However, thickness of deposited PZT-HPTF or deposition rate was decreased about 45%. Standard deviations of the material properties and thickness could be suppressed. Therefore, we think that properties of PZT-HPTF could be improved by pretreatment of Ti substrate with hydrogen peroxide.

Table II Material properties of PZT polycrystalline films deposited on Ti substrates with and without pretreatment using hydrogen peroxide

Item	without pretreatment		with pretreatment	
	Averaged value	Standard deviation	Averaged value	Standard deviation
Film thickness (mm)	6.9	3.5	3.1	0.9
Density (g/cm^3)	2.9	1.0	4.6	0.4
Young's modulus: (x 10^{10}N/m ^{2})	1.9	5.3	3.4	6.7
Piezoelectric constant d_{31} (pC/N)	-27	-	-97	-

CONCLUSION

Problems in the material properties of deposited PZT hydrothermal polycrystalline thick film on the Ti substrate were improved by pretreatment of the substrate using hydrogen peroxide as follows,

1. Hydrophilic property on the surface of Ti substrate was improved.
2. Surface of PZT hydrothermal polycrystalline thick film without pinholes was obtained.
3. Values of density, Young's modulus and piezoelectric constant d_{31} were increased.
4. Standard deviation of thickness and deposited properties could be suppressed.

REFERENCES

1, M. Ishikawa, M. K. Kurosawa, A. Endo, S. Takeuchi, Proc. Symp. Ultrason. Electron., 25, 61-62, (2004)

2. N. Katsura, M. Ishikawa, T. Sato, M. Takeuchi, N. Kawashima, S. Takeuchi, M. Kurosawa, Proceedings of 2003 IEEE International Ultrasonics Symposium 2003). pp.122-123

3. M. Ishikawa, M. K. Kurosawa, A. Endo, S. Takeuchi, 2004 IEEE International Ultrasonics, Ferroelectrics, and Frequency Control Joint 50th Anniversary Conference, Montreal, 2004), pp.902-905

4. Y. Ohba, PhD. Thesis, Tokyo Institute of technology, 1996.

5. Y. Ohba, M. Miyauchi, T. Tsurumi and M. Daimon; *Jpn. J. Appl. Phys.* 32, Part1, 9B, 4095(1993)

6. T. Morita, T. Kanda, Y. Yamagata, M. Kurosawa and T. Higuchi; *Jpn, J. Appl. Phys.,* 36, Part1, 5B, 1997

7. S. Euphrasie, S. Daviero-Minaud and P. Pernod ; Materials Science and Engineering, B104 (2004)

Mater. Res. Soc. Symp. Proc. Vol. 872 © 2005 Materials Research Society J1.4

Micromirror Arrays for High Temperature Operation

Mahmoud F. Almasri and Bruno A. Frazier
Georgia Institute of Technology, Atlanta, GA 30332

ABSTRACT

This paper describes the design, modeling, fabrication, and testing of electroplated metal electrostatic torsion micromirror arrays. The goal is to develop novel micromirror arrays optimized for high temperature operation for use in epitaxial growth systems such as MOCVD and MBE to define device structure and hence eliminate the need for etching and lithography. The metallic micromirror arrays were fabricated with a hexagonal shape and with diameters of 0.5 mm^2 and 1mm^2. The micromirror arrays were structurally composed of primarily electroplated nickel, a mechanically durable material with a high glass transition temperature and with controllable residual stress. The torsion beam was designed with a straight bar and serpentine shape in order to optimize the voltage necessary to tilt the micromirror by ± 10°. A finite element model built in Ansys has been employed to determine the micromirror geometries and performance. A voltage of 130 volts was required to rotate the mirror with a serpentine shape beams by 10°. In addition, the mirror was operated at a resonant frequency of 2.2 kHz.

INTRODUCTION

Micromachined mirrors with electrostatic actuation have been researched extensively over the past several years and used in wide range of applications such as projection display [1,2,3], maskless lithography [4,5], optical scanner [6], switches and optical cross-connects for telecommunication networks [7,8]. The micromirror arrays have been fabricated using surface micromachined polycrystalline silicon [9], and bulk micromachining of silicon on insulator (SOI) [10,11].

The 1-D micromirror is rotated around the rotation axis by applying electrostatic voltage between the mirror surface and one of its electrodes. In static equilibrium, the micromirror is stable over a range of rotation angle since the mechanical torque and the electrostatic torque are equalized. As the voltage is increased slightly above a certain voltage, the electrostatic torque overcomes the mechanical torque and hence the mirror becomes unstable and pulls-down rapidly until its edge touches the substrate. In order to prevent this pull-in behavior, the mirror rotation should be between one-third and one-half of the mirror snap-down angle [12].

In this paper, micromirror arrays are fabricated using electroplated nickel and surface micromachining. The key feature of this structure is that the micromirror arrays can operate at high temperature and achieve high reflectivity while retaining surface flatness. In addition, electrostatic actuation was chosen because it offers many advantages for scanners including fast response time and simple drive electronics.

Design and Modeling

The micromirror arrays consist of either 5×5, 16×16, and 1×16 elements. Each micromirror is designed with a hexagonal shape and has a diameter of 0.5 mm and 1.0 mm. The main reasons for choosing a hexagonal shape mirror are based on the expectation that the angled end of the mirror may help to improve the electrostatic field distribution and hence lower the electrostatic voltage. In addition, the hexagonal shape will allow the mirror array to have high fill factor in comparison to a circular shape array and uniform stress distribution in comparison with a square mirror. The 16x16 micromirror array is individually addressed by rows and columns fabricated from two metal layers while the 5x5 and 1x16 micromirror arrays are individually addressed by a single metal layer. Each mirror is also designed with circular dimples in order to control the maximum tilt angle and prevent an electrical short circuit between the mirror and the bottom electrode. A schematic of the torsional micromirror structures are shown in Figure 1.

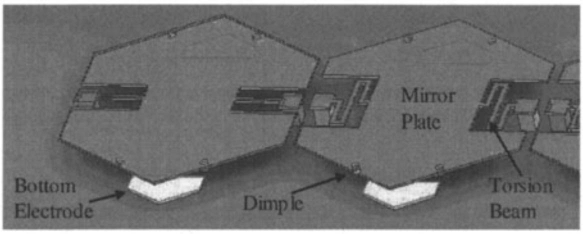


Figure 1. The 3-D view of torsional micromirror geometries with straight bar and serpentine shape beams. The micromirror consists of a nickel electroplated surface, torsion beams, dimple and anchors. The bottom electrode is fabricated from sputtered gold.

Finite element analysis using ANSYS/Multiphysics simulation package has been employed to determine the micromirror geometries and to provide accurate prediction of their static and dynamic performance. A reduced order modeling (ROM) method is used in order to efficiently solve coupled-field problems involving flexible (micromirror) structures. In this model, an input text file is used where the design parameters can be easily changed.

The torsion beams are designed with either a serpentine and straight bar geometry as shown in Figure 1. The serpentine beam has longer length and is less sensitive to the beam width than the straight bar beams. Therefore, a lower actuation voltage is achieved with the serpentine type. The two models show that a voltage of 130 volts and 210 volts, respectively, are required to rotate the mirror by 10°. The results are plotted in Figure 2. In addition, the serpentine shape

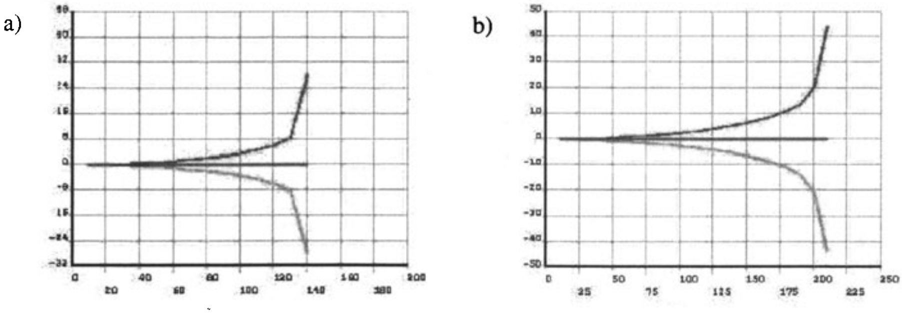


Figure 2. Voltage characteristic of the micromirror with a) a serpentine and b) straight bar beam.