Ceramics International 30 (2004) 1811–1813

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Micro-patterning of sol–gel-derived PZT thin film with SAM

Hisao Suzuki [a,*], Takayuki Mori [a], Tatsuo Fujinami [a], Toshitaka Ota [b], Masayoshi Fuji [b], Minoru Takahashi [b]

[a] *Department of Materials Science, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan*
[b] *Ceramic Research Laboratory, Nagoya Institute of Technology, 10-6-29 Asahigaoka, Tajimi Gifu 507-0071, Japan*

Received 1 December 2003; received in revised form 18 December 2003; accepted 22 December 2003

Available online 31 July 2004

Abstract

Micro-patterns of $Pb(Zr_{0.53}\ Ti_{0.47})O_3$, PZT, thin films with a morphotropic phase boundary (MPB) composition were prepared from molecular-designed PZT precursor solution by using self-assembled monolayer (SAM) as a template. This method includes deposition of SAM followed by the optical etching by exposing the SAM to the UV-light, leading to the patterned SAM as a selective deposition template. The pattern of SAM was formed by irradiating UV-light to the SAM on substrate through a metal mask for the selective deposition of patterned PZT precursor films from alkoxide-derived precursor solution. As a result, patterned ferroelectric PZT films with good electrical properties in micrometer size could be successfully deposited.
© 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: D. Lead zirconate titanate (PZT); Micro-patterning; Self-assembled monolayer (SAM); Chemical solution deposition (CSD); Ferroelectricity; Thin films

1. Introduction

Lead zirconate titanate (PZT) thin films have been attracting worldwide interests in exploring their potential properties [1–3] or the origins [4–6] of their excellent dielectric, ferroelectric and piezoelectric properties near the morphotropic phase boundary (MPB). PZT thin films are expected to apply to the memory devices and micro electro mechanical system (MEMS). Advancement of the nanotechnology requires the ultrafine processing to develop novel devices, and wet etching through the register [7], reactive ion etching [8], sputtering through the mask [9], electron beam lithography [10], laser cutting [11] and others are proposed for ultrafine processing of thin films. However, these techniques are relatively complex and, therefore, are expensive as well as the problem for etching rate. Thus, we propose a novel ultrafine processing for selective deposition of thin films on intended area on a silicon wafer in micrometer size. This method includes deposition of self-assembled monolayer (SAM) [12]. SAM is a organic molecule film covering solid surfaces spontaneously with well-ordered and oriented molecules, exposing specific functional groups outside which can modify surface properties. This paper describes the deposition of patterned PZT films using a novel SAM molecule with both fluoride chain and thiol group in one molecule. We also focus the electrical properties of the resultant patterned PZT films so as to assess the applicability for devices.

2. Experimental procedures

In this study, the SAM molecule, $CF_3(CF_2)_5C_{13}H_{24}O_2SH$, with fluoride chain and thiol group in one molecule was used to control the wettability of a silicon wafer with a platinum electrode. This molecule was synthesized by the dehydration condensation between 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol and 11-mercaptoudecanoic acid using *N*,*N*-dicyclohexylcarbodiimide as dehydration reagent.

Trihydrated lead acetate, titanium iso-propoxide and zirconium *n*-propoxide were used as starting materials, and absolute ethanol was used as a solvent to prepare the CSD precursor solution. The Zr/Ti ratio was fixed at 53/47, and excess Pb (20 mol%) was added to the precursor solution. A nominal composition of the precursor solution was equiva-

* Corresponding author. Tel.: +81-53-478-1157; fax: +81-53-478-1157.
E-mail address: suzuki@eng.shizuoka.ac.jp (H. Suzuki).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.113

lent to that of $Pb_{1.2}(Zr_{0.53}Ti_{0.47})O_3$. Details of the preparation of the precursor solution are described elsewhere [13]. The concentration of the PZT precursor solution was controlled at 0.5 M.

Patterning of the PZT thin films was carried out using a SAM molecule and the PZT precursor solution. At first, Pt(1 1 1)/Ti/SiO_2/Si substrate was dipped into a SAM precursor solution. Then, the SAM template was formed by exposing a SAM film to the ultraviolet light through a metal mask (SAM patterning process). After SAM patterning process, a PZT precursor film was dip-coated on the SAM template. A sequence of SAM patterning process, dip coating of a PZT precursor film, drying at 115 °C, pyrolysis at 350 °C for 10 min of a patterned PZT precursor film were repeated to increase the film thickness (patterning process). Final annealing was performed at 700 °C for 2 h in air.

Crystalline phase in the patterned PZT thin film was identified by X-ray diffraction (XRD). For electrical measurement, Au top electrode was sputtered through a metal mask with 100 μm diameter of the arrayed pinholes. Dielectric behavior of the patterned PZT thin film was measured by a LCR meter (HP-4284A). *P–E* hysteresis loops for the resultant patterned films were measured by a RT6000S (Radiant Technology Inc.).

3. Results and discussion

3.1. Deposition of patterned PZT films

Fig. 1 shows the optical microscope image of patterned PZT thin films. As shown in Fig. 1, uniformly arrayed 700 μm × 700 μm of patterned PZT thin film could be successfully deposited on the silicon wafer with Pt electrode. The deposited PZT patterns exhibited same shape and size as that of the metal mask used. This result exhibited the high potential of $CF_3(CF_2)_5C_{13}H_{24}O_2SH$ SAM molecule as a SAM template, and this SAM molecule has the following three excellent features: (1) SH group in a SAM molecule reacts easily with metal to form strong chemical bonding. In case of this study, SAM forms only by dipping the substrate in $CF_3(CF_2)_5C_{13}H_{24}O_2SH$ solution because SH group

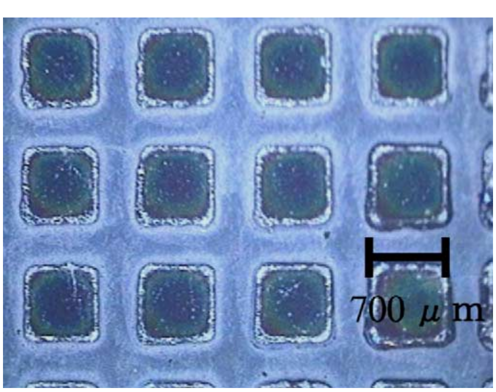
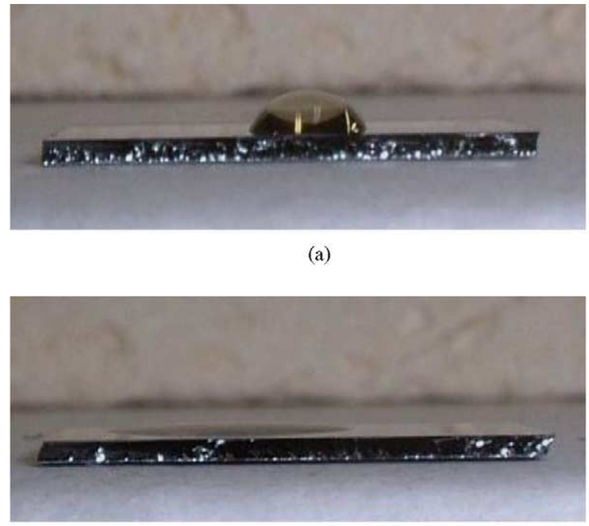


Fig. 1. Optical microscope image of a patterned PZT film.



(a)

(b)

Fig. 2. Appearance of a PZT precursor solution on the substrate with and without SAM, showing the difference of wettability. (a) PZT precursor solution on a $CF_3(CF_2)_5C_{13}H_{24}O_2SH$ SAM template. (b) PZT precursor solution on a substrate after the irradiation of ultraviolet light.

reacts platinum as electrode on the surface of a substrate [14]. (2) Although the mechanism of the chemical adsorption of the sulfur on the surface of metal is not well understood, it has been proposed that an organic compound adsorbs as metal thiolate (RS^-M^+) on metal surface [15,16]. This chemical bonding can easily decompose by irradiating the ultraviolet light because the energy of ultraviolet light exceeds that of the chemical bonding for a metal thiolate [17]. Therefore in this study, Pt–S chemical bonding also can be decomposed by the irradiation of the ultraviolet light, leading to the easy formation of a patterned SAM template by ultraviolet light irradiation through the metal mask. (3) The third feature is the suppression of chemical reaction between a PZT precursor solution and a Pt electrode due to a surface fluoride chain. The contact angle of the PZT precursor solution on a $CF_3(CF_2)_5C_{13}H_{24}O_2SH$ SAM was 68° (Fig. 2(a)), which was measured by a sessile drop method. On the other hand, the contact angle of the PZT precursor solution on the substrate after the irradiation of the ultraviolet light was 8° (Fig. 2(b)). Because a SAM molecule was completely decomposed after pre-annealing at 350 °C, the same SAM template and the same PZT precursor pattern could be easily deposited repeatedly to increase the thickness of the patterned PZT thin film by repeating the patterning process.

3.2. Crystalline phase

Fig. 3 shows the XRD pattern for the patterned PZT film. The XRD pattern shows a perovskite structure except for the Pt(1 1 1) and Pt(2 0 0) peaks. This result shows that patterned PZT thin film of a single phase perovskite structure with mainly (1 1 1)-orientation could be successfully deposited by this patterning process and a SAM template did not affect

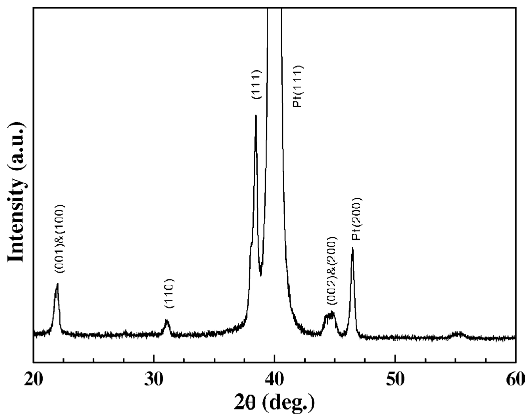


Fig. 3. XRD pattern for a patterned PZT film.

both on the crystal structure and a film orientation, because a SAM molecule decomposed completely before crystallization of a perovskite PZT. Film orientation was same as that of the non-patterned PZT film because of the formation of a Pt–Pb alloy as a in situ seeding layer [18].

3.3. Dielectric and ferroelectric properties

Figs. 3 and 4 show the dielectric and the ferroelectric properties for the patterned PZT film, together with those for the non-patterned PZT film by comparison. As shown in Fig. 3, dielectric behavior of the patterned PZT thin film was almost same as that of the non-patterned PZT thin film except for the relatively large loss at low frequencies. This may be ascribed to the increased grain boundaries. Non-patterned PZT thin film was deposited from same solution and by same annealing process. Therefore, these results indicated that a high potential for a micro-patterning with SAM was confirmed as well as by the *P–E* hysteresis loops for the patterned and non-patterned PZT films in Fig. 4, showing almost same ferroelectric properties (Fig. 5). These results demonstrates that micro-patterning of PZT thin films with SAM as a template using a novel $CF_3(CF_2)_5C_{13}H_{24}O_2SH$ molecule is very promising as a novel and easy fine processing technique for oxide thin films with chemical solution deposition (CSD).

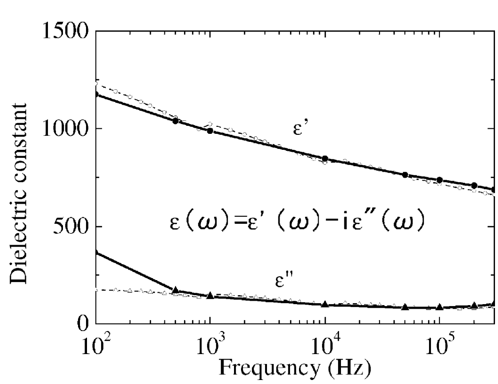


Fig. 4. Dielectric behavior for the patterned and non-patterned PZT films. Solid line: patterned PZT film; dotted line: non-patterned PZT film.

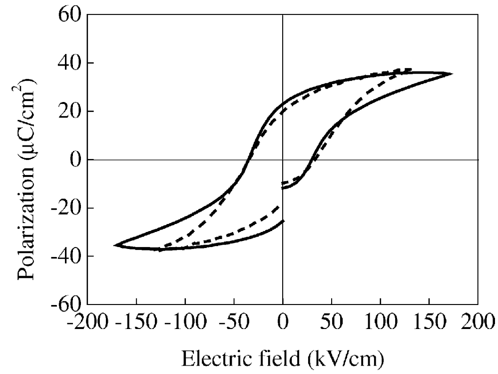


Fig. 5. Ferroelectricity for the patterned and non-patterned PZT films. Solid line: patterned PZT film; dotted line: non-patterned PZT film.

4. Conclusions

By using $CF_3(CF_2)_5C_{13}H_{24}O_2SH$ as a SAM molecule, patterned PZT film with a MPB composition was successfully deposited in micrometer size easily through all wet processing. The resulting PZT micro-pattern exhibited almost same and excellent dielectric and ferroelectric properties as those for the non-patterned PZT film. Therefore, it is concluded that patterning with SAM is very promising for a novel processing not only for PZT but also other films with CSD.

References

[1] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, London, 1971, pp. 91–108.
[2] D. Damijanovic, Rep. Prog. Phys. 61 (1988) 1267–1324.
[3] X.H. Du, J. Zheng, U. Belegundu, K. Uchino, Appl. Phys. Lett. 72 (1988) 2421–2423.
[4] L. Bellaiche, D. Vandderbilt, Phys. Rev. Lett. 83 (1999) 1347–1350.
[5] R. Guo, L.E. Cross, S.E. Park, B. Noheda, D.E. Cox, G. Shirane, Phys. Rev. Lett. 84 (2000) 5423–5426.
[6] B. Noheda, D.E. Cox, G. Shirane, R. Guo, B. Jones, L.E. Cross, Phys. Rev. B 63 (2000) 14103–141012.
[7] H. Kueppers, T. Leuerer, E. Monkwa, Sens. Actuators A 97–98 (2002) 680–684.
[8] R. Suchaneck, R. Tews, G. Gerlach, Surf. Coat. Technol. 116–119 (1999) 456–460.
[9] J. Akiwase, Ouyoubuturi 68 (1) (1999) 44–47.
[10] C. Alexe, M. Haragea, A. Visinoiu, Scripta Mater. 44 (2000) 1175–1179.
[11] K. Li, D.W. Zeng, K.C. Yung, Mater. Chem. Phys. 75 (2002) 147–150.
[12] A. Ulman, Chem. Rev. 96 (1996) 1533–1554.
[13] H. Suzuki, T. Koizumi, Y. Kondo, S. Kaneko, J. Eur. Ceram., Soc. 19 (1999) 1397–1401.
[14] C.D. Bain, E.B. Troughton, J. Am. Chem. Soc. 111 (1989) 321–335.
[15] G.M. Whitesides, P.E. Labinis, Langmuir 6 (1990) 87–96.
[16] L.H. Dubois, R.G. Nuzzo, Ann. Rev. Phys. Chem. 43 (1992) 437–463.
[17] H. Sugimura, O. Takai, Surf. Sci. 22 (6) (2001) 364–369.
[18] H. Suzuki, Y. Kondo, S. Kaneko, T. Hayashi, Mater. Res. Soc. Symp. Proc. 596 (2000) 241–246.