

## Sol-gel Mechanism of Self-patternable PZT Film Starting from Alkoxides' Precursors

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### ABSTRACT

Sol-gel preparation technique using a chemical reaction of metal alkoxides has been widely used for the fabrication of various materials including ceramics. However, its mechanism has been studied till now because a number of chemical ways are possible from various alkoxides and additives. In this study, the mechanism of hydrolysis, condensation, and polymerization of alkoxides were investigated from the fabrication of lead-zirconate-titanate ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ; PZT) thin film that is used as various micro-actuator, transducer, and sensor because of its high electro-mechanical coupling factors and thermal stability. Furthermore, the fabrication process and characteristics of self-patternable PZT film using photosensitive stabilizer were studied in order to resolve the problem of physical damage and properties degradation during dry etching for device fabrication. Using an optimum condition to prepare the self-patternable PZT film, more than 5000 Å thick self-patternable PZT film could be fabricated by three times coating. The PZT film showed 28.4  $\mu\text{C}/\text{cm}^2$  of remnant polarization ( $P_r$ ) and 37.0 kV/cm of coercive field ( $E_c$ ).

**Key words :** Sol-gel, Self-patterning, PZT, Photosensitizer, UV exposure

## 1. Introduction

Sol-gel process contains fractal geometry and percolation theory in physics, hydrolysis and poly-condensation mechanism in chemistry, sintering and structural relaxation in ceramics, and so on. When sol is prepared with starting materials of molecular unit, a solid fractal network is obtained through hydrolysis and poly-condensation reaction. Then an improved properties of ceramic could be obtained by removing inhomogeneity in materials through the control of chemical reaction concerning with inorganic polymerization.<sup>1)</sup> One of dielectric material with high dielectric constant which could be successfully prepared by sol-gel procedure,  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (PZT) piezo-ceramic is known as a key material for non-volatile memory, micro-sensor, actuator, and IR-sensor, especially for Micro-Electronic Mechanical System (MEMS) recently.<sup>2,3)</sup> Furthermore in order to overcome the degradation problem induced from the dry etching for micro-patterning of system device, a self-patterning of the film using photosensitive precursor has been studied.<sup>4-7)</sup>

In this study, a mechanism of self-patternable PZT film formation by sol-gel using photosensitive stabilizer was studied and the ferroelectric properties of self-patterned PZT film were compared with those of conventionally prepared by sol-gel procedure.

## 2. Theory

### 2.1. Metal Alkoxides

Metal alkoxides of  $\text{M}(\text{OR})_2$  chemical formula, usually called as alcoholates, are produced by direct or indirect chemical reaction between metal, M and alcohol, ROH. A number of chemical forms of alkoxides are possible for a certain metal, as shown in Table 1, as various chemical forms are possible for alcohol. It is not obvious to know the exact chemical formula formed during sol-gel chemical reaction. However, it is possible to estimate that the oxygen in alkoxy and OR groups acts as electron pair donor from the reaction with other metal. Unlike weak covalent bond, alkoxy group could form a direct bond with other metal under a certain condition.<sup>8)</sup>

Alkoxides are very reactive with moisture, heat, and light and an organic decomposition in alkoxides could happen with them. The alkyl group must stabilize the alkoxide so that it is enough volatile for the M-OR and MO-R bonds to break to liberate a free oxide. In general, metal alkoxide is very reactive from the high electronegativity of OR system and this high reactivity can stabilize M with its highest oxidation state and metal, M becomes to be very sensitive to nucleophilic attack.<sup>1)</sup>

Till now, the reaction mechanism proposed by Livage<sup>9)</sup> has been generally accepted: the first step, one of alkoxy group is rapidly replaced by nucleophilic mechanism during hydrolysis reaction and the second step, hydroxo (or ol) or oxo-bridges are formed by condensation reaction. However the chemical reaction of metal alkoxide strongly depends on

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**Table 1.** Nomenclature of Alkoxides  $M(OR)_n$ <sup>8)</sup>

Alcohol R(OH)	Alkoxy ligand to the metal M	Alkoxide	Abb. for OR
Methanol CH <sub>3</sub> OH	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{O}-\text{M} \end{array}$	methoxide	OMe
Ethanol C <sub>2</sub> H <sub>5</sub> OH	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{O}-\text{M} \\   \\ \text{H} \end{array}$	ethoxide	OEt
1, propanol (n-propanol) C <sub>3</sub> H <sub>7</sub> OH	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{M} \\   \\ \text{H} \end{array}$	1-propoxide (n-propoxide)	OPr <sup>i</sup>
2, propanol (iso-propanol) C <sub>3</sub> H <sub>7</sub> OH	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{M} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	2-propoxide (iso-propoxide)	OPr <sup>s</sup>
1, Butanol (n-butanol) C <sub>4</sub> H <sub>9</sub> OH	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{M} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	1-butoxide (n-butoxide)	OBu <sup>n</sup>
2, Butanol C <sub>4</sub> H <sub>9</sub> OH	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-\text{M} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad   \\ \quad \quad \quad \quad \text{O} \\ \quad \quad \quad \quad   \\ \quad \quad \quad \quad \text{M} \end{array}$	2-butoxide (sec-butoxide)	OBu <sup>s</sup>
2, methylpropanol (iso butanol) C <sub>4</sub> H <sub>9</sub> OH	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-\text{M} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad   \\ \quad \quad \quad \quad \text{O} \\ \quad \quad \quad \quad   \\ \quad \quad \quad \quad \text{M} \end{array}$	2-methylpropoxide (iso-butoxide)	OBu <sup>i</sup>
2, methylprop, 2, ol (tertio butanol) C <sub>4</sub> H <sub>9</sub> (OH)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{M} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad   \\ \quad \quad \quad \text{C} \\ \quad \quad \quad   \\ \quad \quad \quad \text{H} \end{array}$	tertio butoxide	OBu <sup>t</sup>

R: hydrocarbon radicals C<sub>n</sub>H<sub>2n+1</sub>

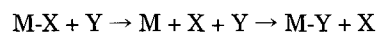
starting molecular type, a completely different type of hydrolysis and condensation could form a new material. The control of sol-gel reaction can be achieved by using chemical additives; the reactivity of new ligand in hydrolysis and the electronic distribution of formed molecule and the coordination number of metal atom will be the most important variables.<sup>10)</sup>

## 2.2. Transformation Mechanism of Complexes

Various metals and molecules named ligands may bind to complex and cation M either directly or through the substitution with other ligand. This transformation mechanism shows different characteristic due to the difference in partial charge of atoms, especially negative partial charge is called as nucleophilic and positive partial charge as electrophilic.<sup>9)</sup> Chemical bonding induced from the electronic distribution of atom is understood by a partial charge model<sup>1,8,10)</sup> as calculated as  $\delta_i$ , the charge of each atom in molecule and electron moving is derived from the difference in electronegativity of atoms.<sup>11)</sup> By this model, the electronegativity  $X_i$  of an atom changes linearly with partial charge  $\delta_i$  and electron transfer is stopped when the electronegativity values for all of atoms have the same value as mean electronegativity.

The addition of ligand happens when the coordination number of the cation in complex is not fully occupied and the other cases, the substitution occurs. The substitution can be done one of three mechanism; dissociative, associative, and interchange substitutions.

In the dissociative substitution mechanism, X ligand becomes very unstable state after breaking the bond between leaving group, X and complex with enough thermal energy. Finally an intermediate phase is formed with reduced coordination number for metal M, and then the coordination number of cation M is satisfied with entering group, Y.



The rate constant of the reaction is independent on the concentration of Y ligand and this kind of dissociative mechanism is called unimolecular nucleophilic substitution, S<sub>N</sub>1.

In the associative substitution mechanism, an intermediate phase with increased coordination number forms by binding with entering group Y before departure of the other ligand.<sup>12)</sup> The rate constant of the reaction depends on the concentrations of entering Y ligand and leaving X ligand. This reaction mechanism is called as bimolecular nucleophilic substitution, S<sub>N</sub>2.

philic substitution,  $S_N2$ .



In the interchange substitution mechanism, the coordination number of metal M is increased or decreased without the formation of intermediate phase and the reaction proceeds in one step. The substitution is called  $S_N2$  substitution.

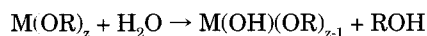
As described above, the addition corresponds to the case of bonding with new ligand Y to satisfy the coordination number of metal M and this leads the M to be stable. This is expressed as nucleophilic addition  $A_N$ .



### 2.3. Hydrolysis and Condensation Mechanisms of Metal Alkoxide

Till now the thermal, electronic, and structural studies on the hydrolysis and condensation reaction of metal alkoxide have been proceeded and the effect of additives on the reaction has been carried out recently.<sup>13-16</sup> However, the basic reaction mechanism could be described as hydroxo(ol), OH, and oxo ligand is formed during the hydrolysis, then the condensation reaction is induced. The additives have been used to control the reaction and actually is involved in the reaction.

During the hydrolysis, the alkoxy group (OR) turns to be hydroxo ligands (OH) or oxo ligands (O), and this changing reaction depends on the characteristics of alkyl group and solvent, concentration of each constituent in solvent, molar ratio  $r_w$  of  $H_2O$  and alkoxy, and temperature. During the hydrolysis, one of alkoxy groups reacts with water and forms hydroxo ligand.



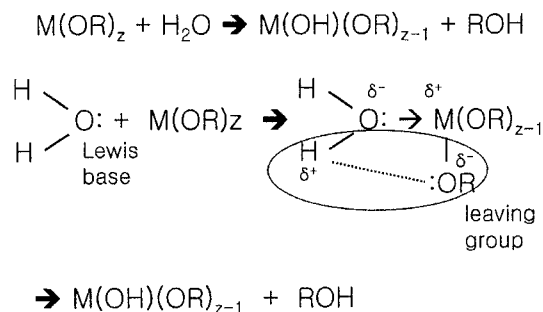
The mechanism of hydrolysis consists in a nucleophilic substitution where water molecule reacts with alkoxide and as a result, the reaction rate strongly depends on the kind of alkoxide. In this reaction, the difference due to the chemical characteristic of each alkoxide can be explained with partial charge model. Several kinds of partial charge of metals in alkoxides are given in Table 2. As given in the table, metal M is electrophile ( $\delta(M) > 0$ ) and oxygen is nucleophilic ( $\delta(O) < 0$ ). In some cases, a living group may possess positive partial charge and then an intermediate phase could be formed. In most cases, living groups are alcohol (ROH,  $\delta(ROH) > 0$ ) or water molecule ( $H_2O$ ,  $\delta(H_2O) > 0$ ). Besides, the molecular complexity depends on the nature of metal atom. Within a particular group, it increases with the atomic size

**Table 2.** Positive Partial Charge  $\delta(M)$  for Metals in Various Alkoxides<sup>1)</sup>

Alkoxides	Zr(OEt) <sub>4</sub>	Ti(OEt) <sub>4</sub>	Nb(OEt) <sub>5</sub>
$\delta(M)$	+0.65	+0.63	+0.53
Ta(OEt) <sub>5</sub>	W(OEt) <sub>3</sub>	W(OEt) <sub>6</sub>	Si(OEt) <sub>4</sub>
+0.49	+0.46	+0.43	+0.32

**Table 3.** Molecular Complexity (Number of Metal Atoms Per Osmotic Molecule) of Some Transition Metal Ethoxides as a Function of Metal Size<sup>1)</sup>

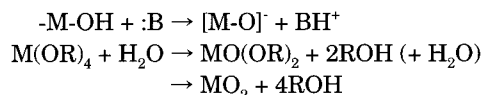
Compound	Ti(OEt) <sub>4</sub>	Zr(OEt) <sub>4</sub>	Hf(OEt) <sub>4</sub>	Th(OEt) <sub>4</sub>
Covalent radii(Å)	1.32	1.45	1.44	1.55
Molecular complexity	2.9	3.6	3.6	6.0



**Fig. 1.** Mechanism of hydrolysis forming hydroxo ligand, illustrated in diagram.<sup>8)</sup>

of metal as shown in Table 3. Water and alkyl group are important factors for hydrolysis, especially bonding state of alkyl group because if alkyl group is long, the breaking of O-R bond becomes to be difficult and the reaction rate of hydrolysis decreases. This mechanism is schematically given in Fig. 1.

In the formation process of oxo ligands, Lewis bases with strong nucleophiles deprotonate OH ligands of metal M and M forms an acidic oxide.<sup>17)</sup> :B is Lewis base like  $OH^-$  or  $NH_3$ .

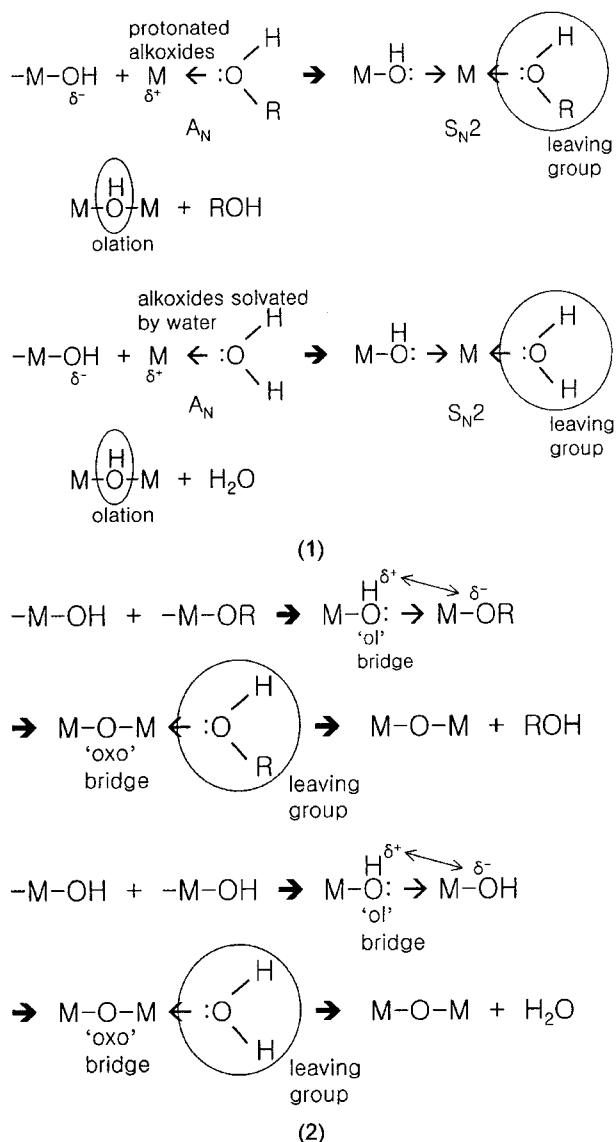


The condensation reaction is preceded by olation or oxolation reaction. The condensation by olation reaction is represented with  $S_N2$  nucleophilic substitution mechanism, and contains two steps. In the first step, the reaction is preceded by nucleophilic addition and at the second step; olation is formed by  $S_N2$  mechanism with departure of leaving group. As shown in Fig. 2(1), the living group can be an alcohol molecule by protonated alkoxy ligand or water molecule by solvated alkoxide.

In the condensation reaction of alkoxide oxolation, ol-bridge is formed at first and turns to be oxo-bridge, that is, hydrogen of ol-bridge moves to terminal alkoxy(OR) ligand or other hydroxo(OH) ligand and form oxo-bridge as shown in Fig. 2(2).

## 3. Experimental Procedures

To make self-patternable PZT film used by sol-gel method, metal alkoxides of Zirconium N-Butoxide(ZNB) and Titanium Iso-Propoxide(TIP) were dissolved in ethanol solvent



**Fig. 2.** (1) Mechanism of condensation forming ololation and (2) Mechanism of condensation forming oxolation, illustrated in diagram.<sup>1,8)</sup>

with lead acetate tri-hydrate. 0.5 M concentration of PZT starting precursor was prepared with Zr/Ti ratio of 52/48 at which there is Morphotropic Phase Boundary(MPB). This region in PZT system has the dielectric constant and piezoelectric coefficients enhanced due to the metastable coexistence of tetragonal and rhombohedral phases resulting in the maximum poling efficiency and the electromechanical activity.<sup>18)</sup> 15 mol% of excess Pb to compensate Pb loss during high temperature annealing, and Diethanolamine(DEA) as a stabilizer was added to restrain hydrolysis by hydrophilic of the alkoxides. Successively, o-nitrobenzaldehyde (NBAL) sensitive to UV wavelength on 300–400 nm was added to cross-link metal alkoxides through photoreaction. Then the complex solution was stirred for 24 h.

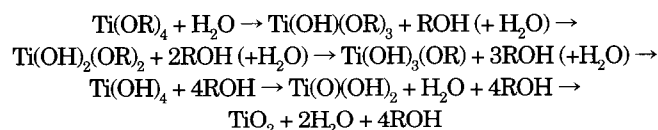
After stirring it enough, the PZT precursor solution was deposited on platinum-coated silicon substrate by spin coat-

ing at 3500 rpm for 20 s and dried on a hot plate at 60 for 2 min. Then UV light with 365 nm wavelength was irradiated on the spin-coated photosensitive precursor film using negative mask for patterning of the film after wet etching. After intermediate anneal to remove organic ligand completely, the film was finally annealed at 650 for 45 min under O<sub>2</sub> atmosphere by a direct insertion to a furnace. The above coating process was repeated for 3 times coating to obtain a thick film. Pt was sputter-deposited for top electrode in order to measure the ferroelectric properties.

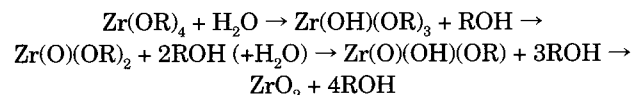
The thermal behavior of PZT gel powder was monitored using thermal gravimeter and differential thermal analysis (TG-DTA), and the change of organic state before and after the heat treatment was monitored using Fourier Transform Infrared Spectroscopy(FT-IR). The surface morphology was observed using Scanning Electron Microscopy(SEM) and Polarization-Voltage(P-E) was measured using RT66A standard ferroelectric test system.

#### 4. Results and Discussion

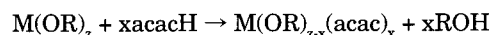
Titanium alkoxides in hydrolysis reaction generally forms hydroxo ligand. As for most other alkoxides, hydrolysis is not only quicker than condensation but also much more exothermic. After the reaction, precipitation and gelation make rapid progress, so it is necessary to control the reaction rate by using a catalyzer or a stabilizer for acceleration or deceleration, respectively.



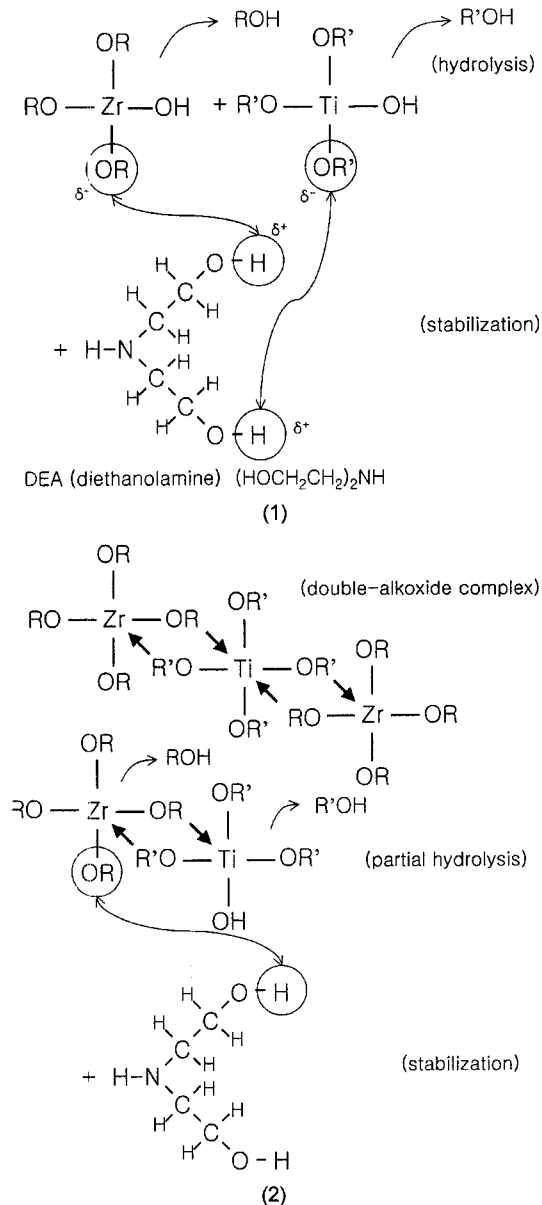
Unlike most other alkoxides, when zirconium undergoes hydrolysis, it is not hydroxo ligands that replace the alkyl groups but either oxo or aqua ones. Such a hydrolysis follows a reaction of the type.



As stated above, as for zirconium alkoxides, hydrolysis being a much quicker reaction than condensation, the solid phase obtained consists of dense hydrated aggregates of zirconium oxide. In order to produce soluble polymeric intermediates, it is obviously necessary to slow down extremely the hydrolysis reaction. The most efficient technique consists of complexing the zirconium alkoxides with a chelating additive such as acetylacetone or diethanolamine in an organic solvent. Then the chelating complex is induced according to the reaction.



In the result, gel particle formed by the reaction grows to oligomer and influences the continuous process such as gelation and sintering so on.



**Fig. 3.** (1) Mechanism of hydrolysis and stabilization of Zr, Ti alkoxides and DEA and (2) Mechanism of partial hydrolysis and stabilization of Zr, Ti alkoxides and DEA.

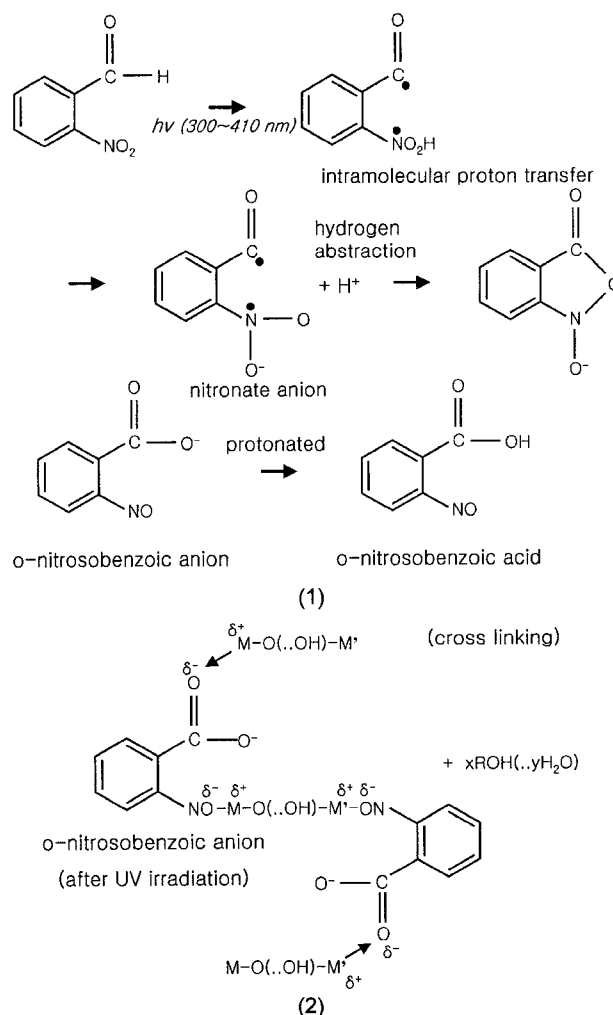
Fig. 3 shows mechanism analysis when different metal alkoxides used in our study, Zirconium N-Butoxide(ZNB) and Titanium Iso-Propoxide(TIP) were mixed with additives. As shown in Fig. 3, it might be divided into two types about reaction mechanism of mixing different alkoxides. In the first part, it is indicated that there are same reaction mechanism although they are different alkoxides. In the second one, different cations spread throughout the sol-gel with a greater homogeneity, so-called double-alkoxides complex<sup>8)</sup> that consist of two metal atoms. Some of those double-alkoxides are simply synthesized by mixing the two initial alkoxides. After this, controlled hydrolysis and stabilization mechanism are considered.

In the continuous step, photosensitizer NBAL for negative

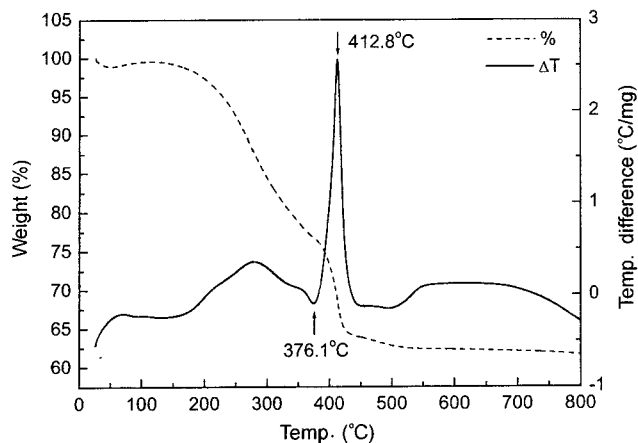
pattern added in the solution to form self-patternable PZT film could be analyzed into the mechanism of photosensitized reaction. Emission is not the only possible fate of the electronically excited state formed in intermolecular energy transfer. Dissociation and chemical reaction are two other important routes for utilization of electronic excitation. Such reactions take place in a species other than the one absorbing the radiation, and sensitization often makes it possible to induce photochemical change in a wavelength region.<sup>19)</sup>

Upon the photoexcitation of NBAL photosensitive on the wavelength of 300~400 nm, the aci-form is rapidly produced through the intramolecular proton transfer reaction and the proton is dissociated to induce the nitronate anion in solution. Consequently the nitronate anion is converted to the o-nitrosobenzoic anion (NS<sup>-</sup>) as shown in Fig. 4(1).

Fig. 4(2) presents photochemical mechanism when UV irradiates PZT film mixed with NBAL. By irradiation, forming of radical and activation from reactant provoke energy transfer and dissociation from metal ions so that cross-link-



**Fig. 4.** (1) A photodissociation reaction of o-nitrobenzaldehyde (NBAL) and (2) Cross-linking mechanism of photoreaction with NBAL and metal alkoxides.

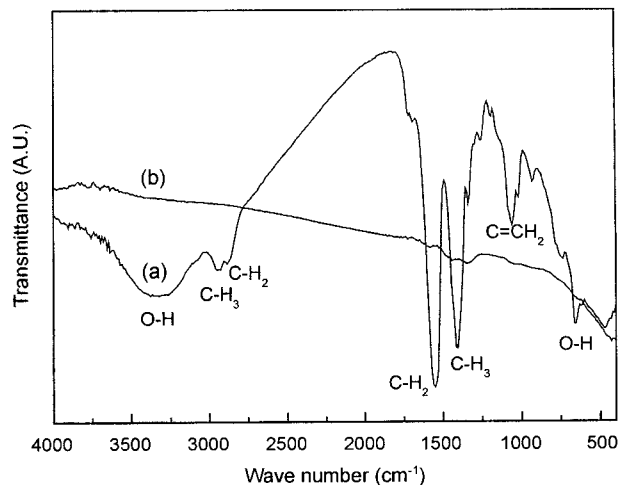


**Fig. 5.** TG-DTA curves of PZT prepared by compounding starting precursors and additives.

ing is produced, and then solubility of gel film reduces with building up the linking chain by condensation.

Fig. 5 shows the TG-DTA curves of the PZT powder after gelled PZT prepared from combining starting precursors and additives was dried completely at 70°C. The heating rate was 2°C/min and the exothermic peak around 413°C with large weight loss corresponds to the decomposition of strong bridging bonds of NBAL and DEA bonding to alkoxides. Therefore, 400°C was set as an intermediate annealing temperature of PZT wet-gel film for organic-removal in the film. Besides, the atmosphere of heat treatment was controlled under O<sub>2</sub> ambient to remove organic effectively, and it was confirmed by FT-IR spectra as shown in Fig. 6.

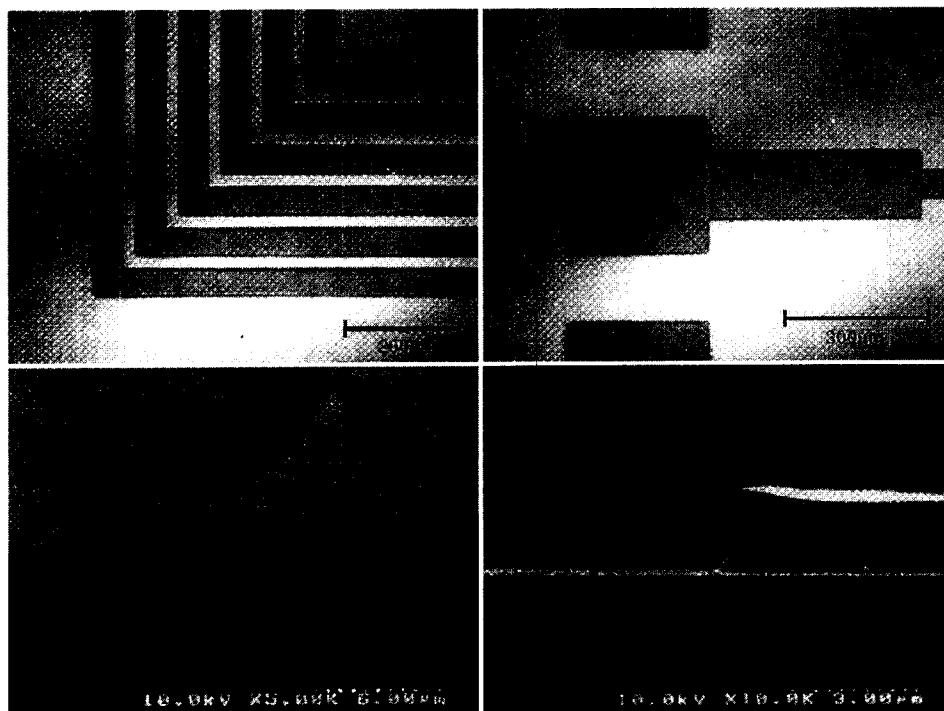
Fig. 7 indicated the images of self-patterned PZT film



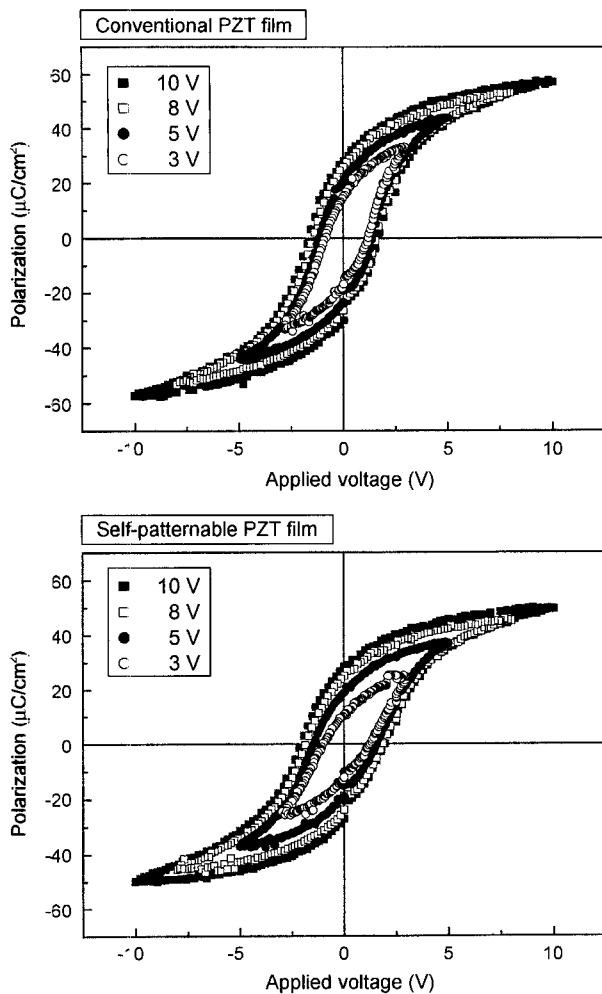
**Fig. 6.** FT-IR spectra of PZT film (a) before and (b) after intermediate anneal under O<sub>2</sub> ambient.

using optical spectroscopy and SEM. Dark area corresponded to the PZT film and bright area to Pt substrate in the figure above. This results in self-patterning was clearly embodied through the mechanism of cross-linking. That is, non-irradiation area was etched with 25 μm width, and it is confirmed that cross-linking reaction in gel film was not accomplished by non-UV irradiation.

Fig. 8 displays Polarization-Voltage(P-V) of self-patternable PZT film with more 5000 Å thickness. The thick film after treated with the intermediate and final anneal exhibited well-defined hysteresis loops and saturated behavior better than loops of conventional PZT as the remnant polar-



**Fig. 7.** Optical images and cross-sectional images of self-patterned PZT films with negative patterns.



**Fig. 8.** Hysteresis loops for conventional and self-patternable PZT films after intermediate and final anneal under  $O_2$  ambient.

ization ( $P_r$ ) and coercive field ( $E_c$ ) values were measured as  $28.4 \mu\text{C}/\text{cm}^2$  and  $37.0 \text{ kV}/\text{cm}$ , respectively. Therefore, PZT film forming self-patterning has a good ferroelectric properties and makes a counterproposal for overcoming problems of etching pattern as well.

## 5. Conclusions

In this work, self-patterning method was used for developing films properties, and we investigated mechanism of metal alkoxides and additives such as a stabilizer, DEA and a photosensitizer, NBAL. Precipitation of sol was suppressed due to the addition of DEA, and stability of the sol was maintained even after NBAL addition. Radical in NBAL, which was generated by UV exposure, played a role of causing cross-linking between metal alkoxides. In the region of non-UV irradiation, it was etched clearly. Consequently, it was revealed that negative pattern type was accomplished by UV irradiation.

Residual organic group was removed by optimizing intermediate annealing condition such as temperature and

atmosphere. By this process, remnant polarization and coercive field for the self-patternable PZT film annealed at  $650^\circ\text{C}$  for 45 min was  $28.4 \mu\text{C}/\text{cm}^2$  and  $37.0 \text{ kV}/\text{cm}$ , respectively.

In this study, processing condition of self-patterned PZT film was optimized, and it is anticipated that self-patterned PZT film could be applicable to the practical system due to enhanced ferroelectric properties.

## Acknowledgement

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## REFERENCES

1. C. J. Brinker and G. W. Scherer, "Sol-gel Science, The Physics and Chemistry of Sol-gel Processing," pp. 21-91, Academic Press, San Diego, 1990.
2. D. L. Polla, "Microelectromechanical System Based on Ferroelectric Thin Films," *Micro. Eng.*, **29** 51-8 (1995).
3. C. C. Hsueh, T. Tamagawa, C. Ye, A. Helgeson, and D. L. Polla, "Sol-gel Derived Ferroelectric Thin Films in Silicon Micromachining," pp. 123-34 in Science and Technology of Intergrated Ferroelectrics 2000. Edited by C. Paz de Araujo, O. Auciello, R. Ramesh, and G. W. Taylor, Gordon and Breach Science Publishers, 2000.
4. M. Alexe, J. F. Scott, C. Curran, N. D. Zakharov, D. Hesse, and A. Pignolet, "Self-patterning Nano-electrodes on Ferroelectric Thin Films for Gigabit Memory Applications," *Appl. Phys. Lett.*, **73** [11] 1592-94 (1998).
5. M. Alexe, A. Gruverman, C. Hamagea, N. D. Zakharov, A. Pienolet, D. Hesse, and J. F. Scott, "Switching Properties of Self-assembled Ferroelectric Memory Cells," *Appl. Phys. Lett.*, **75** [8] 1158-60 (1999).
6. H. Uchida, N. Soyama, K. Kageyama, K. Ogi, M. C. Scott, J. D. Cuchiari, G. F. Derbenwick, L. D. Mcmillan, and C. A. Paz de Araujo, "Characterization of Self-patterned  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  Thin Films from Photo-sensitive Solutions," *Integrated Ferroelectrics*, **16** 41-52 (1997).
7. G. Uozumi, K. Kageyama, T. Atsuki, N. Soyama, H. Uchida, and K. Ogi, "Evaluation of Self-patterned  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  Thin Film from Photosensitive Solution," *Jpn. J. Appl. Phys.*, **38** 5350-53 (1999).
8. A. C. Pierre, "Introduction to Sol-gel Processing," pp. 11-85, Kluwer Academic Publishers, Boston, 1998.
9. J. Livage, M. Henry, and C. Sanchez, "Sol-gel Chemistry of Transition Metal Oxides," *Progress in Solid State Chemistry*, **18** 259-342 (1988).
10. C. Sanchez, J. Livage, M. Henry, and F. Babonneau, "Chemical Modification of Alkoxide Precursors," *J. of Non-Cryst. Solids*, **100** 65-76 (1988).
11. R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, "Electronegativity: The Density Functional Viewpoint," *J. of Chem. Phys.*, **68** [8] 3081 (1978).

12. J. McMurry, "Organic Chemistry," Brooks/Cole, International Thomson Publishing Company, 5<sup>th</sup> Edition, New-York, 2001.
13. N. V. Golubko, M. I. Yanovskaya, and I. P. Romm, "Hydrolysis of Titanium Alkoxides: Thermochemical, Electron Microscopy, Sxas Studies," *J. of Sol-gel Sci. and Tech.*, **20** 245-62 (2001).
14. H. Hayashi, H. Suzuki, and S. Kaneko, "Effect of Chemical Modification on Hydrolysis and Condensation Reaction of Zirconium Alkoxide," *J. of Sol-gel Sci. and Tech.*, **12** 87-94 (1998).
15. M. J. Percy, J. R. Bartlett, L. Spiccian, B. O. West, and J. L. Woolfrey, "The Influence of  $\beta$ -Diketones on the Hydrolysis and Growth of Particles from Zirconium(IV) n-propoxide," *J. of Sol-gel Sci. and Tech.*, **19** 315-19 (2000).
16. H. Honda, K. Suzuki, and Y. Sugahara, "Control of Hydrolysis and Condensation Reactions of Titanium Tert-butoxide by Chemical Modification with Catechol," *J. of Sol-gel Sci. and Tech.*, **22** 133-38 (2001).
17. M. T. Harris, A. Singhal, J. L. Look, J. R. Smith-Kristensen, J. S. Lin, and L. M. Toth, "FTIR Spectroscopy, SAXS and Electrical Conductivity Studies of the Hydrolysis and Condensation of Zirconium and Titanium Alkoxides," *J. of Sol-gel Sci. and Tech.*, **8** 41-7 (1997).
18. B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics*, pp.135-37, Academic Press, London and New York, 1971.
19. R. P. Wayne, *Principles and applications of photochemistry*, pp.100-25, Oxford University Press, New York (1988).