Chemical Processing and Properties of Functional Ceramics

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Abstract:

Functional ceramic films have been receiving great attention because of their potentials for emerging applications, which include integrated sensors, actuators and other devices responding to magnetic, electric, optic and stress fields. Many methods, such as liquid phase epitaxial growth, chemical vapor deposition, molecular beam epitaxial growth, sputtering, laser ablation and chemical solution deposition, have been developed to fabricate thin films with desired properties. Among these methods, the chemical solution deposition method has the advantages of good homogeneity, ease of compositional control, low temperature processing, and large area and versatile shaping with integrated functionalities over vacuum deposition techniques. This paper reviews a part of the authors' results on the chemical processing of some epitaxial ferroelectric, pyroelectric, and piezoelectric films as well as nonlinear optic films. In addition, the processing and properties of nano-sized functional ceramic particles/organic hybrids is presented as an example of novel and promising materials, which are expected to create a emerging area.

1. Introduction

Recently, functional ceramics have been receiving a great deal of attention in the advanced technologies. The studies on processing of ferroelectric, piezoelectric and non-linear optic films have given significant opportunities for developing miniaturized devices in emerging areas.

Systems of $LiNbO_3$, $Pb(Zr,Ti)O_3$ (PZT) and $K(Ta,Nb)O_3$ (KTN) have large electromechanical coupling coefficient, and pyroelectric and electro-optic properties. Thin films with preferred orientation have mainly been fabricated by physical deposition methods and chemical vapor deposition method. On the other hand, the chemical solution deposition (CSD) process has the advantages of feasible control of composition, homogeneity, and shape.[1-14]

Nano-sized functional ceramic particles/organic hybrids have recently been developed as a new family of materials.[15-19] The conventional bending of fine dielectric or magnetic particles into polymer causes the particle agglomeration, leading to the degradation of the properties. The authors have developed a novel method to fabricate the hybrids based on the in-situ nucleation and growth of dielectric particles in an organic matrix below 100°C through the reaction control of designed metallo-organic molecules with combination of the polymerization.

This paper reviews the processing and properties of epitaxial films of $LiNbO_3$, PZT and KTN as well as a novel functional material of $PbTiO_3$/organic hybrids though the chemical solutions.

2. Processing Scheme of thin films

Figure 1 illustrates the general flow diagram for the preparation of electronic ceramics by chemical processing through metal alkoxide solutions. The formation of the intermediate compound, e.g. complex alkoxide, has been mentioned elsewhere in terms of homogeneous solution. The partial hydrolysis of the solution is most critical to manipulate the nature of the precursor chemistry.[12]

The chemical bonds and the coordination state of

alkoxides were analyzed by FT-IR, NMR, UV spectroscopy and gas chromatography (GC). The viscosity and density of the precursor alkoxide solutions were measured with a rotational viscometer and a pycnometer. Alkoxy-derived films were prepared on substrates by a dip-coating method or a spin coating method and then heat-treated in a mixture gas flow of water vapor and oxygen to promote crystallization and the release of carbonates.

The crystallization process of alkoxy-derived films was analyzed by XRD, TEM and FT-IR. Morphologies and structures of film and substrate interfaces were analyzed by Auger electron spectroscopy, Rutherford back scattering, and microscopic observations.

D-E hysteresis loops of films were measured using a modified Sawyer-Tower circuit. Refractive indices were determined by ellipsometry.
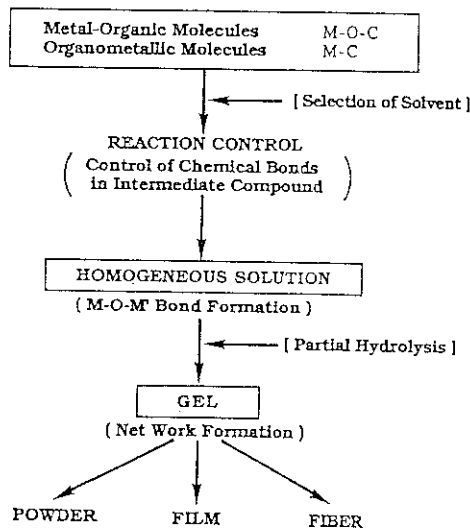

Fig.1 CSD processing of electronic ceramics

3. Ferroelectric and Non-linear LiNbO₃ Thin Films[1-7]

Figure 2 summarizes the key processing factors to synthesize stoichiometric epitaxial LiNbO₃ films at low temperature (below 500°C). Lithium ethoxide is reacted

with niobium ethoxide for 24h, which was followed by FT-IR spectra and NMR spectra[1]. This chemical coordination of ions in a double alkoxide was also confirmed by Eichorst et al.[20].

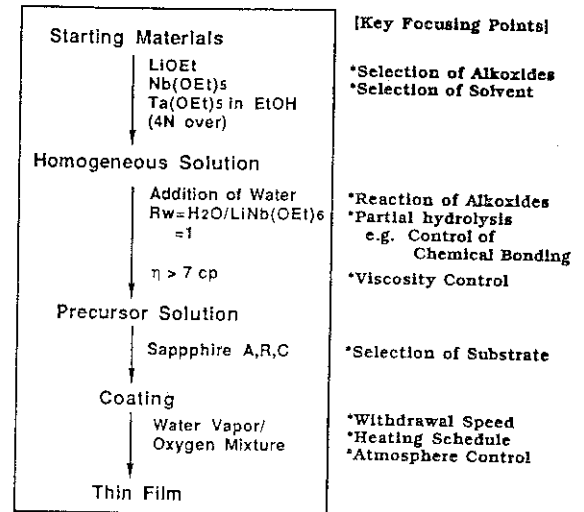Fig.2 Key processing parameters for the processing of LiNbO₃ films

The amount of water addition for the partial hydrolysis influences strongly the crystallization of films. The addition of an equivalent mole of water to $LiNb(OC_2H_5)_6$ and heat treatment of alkoxy-derived films in flow of water vapor and oxygen mixture were found to enhance the crystallization and avoid carbonate formation.

The crystalline films were fabricated above 250°C on various substrates, such as sapphire and Si. The typical linear relationship could be observed between logarithm of withdrawal speed and logarithm of film thickness as crystallized for one dip-cycle. By repeating the dip-coating procedure, the thickness of crystallized films increased lineally without any distinct interface between layers.

Films on sapphire indicated highly preferred orientation at 400°C according to the sapphire orientation, such as (001), (100) and (012). The films carefully crystallized on sapphire substrates exhibited

the epitaxial feature as confirmed by RHEED and X-ray pole figure profile. However, films on Si substrates were polycrystalline. Auger electron spectroscopy and Rutherford back scattering data showed clearly the uniform composition and the sharp interface between film and substrate. No significant interdiffusion of ions was detected.

The authors also have developed the methods to pattern $LiNbO_3$ waveguides using a chemically modified precursor, which is sensible to UV light. The epitaxial films of $LiNbO_3$ processed at 500°C on sapphire substrates exhibit the characters of waveguides and second harmonic wave generation, which lead to the new electro-optic devices.[21,22]

4. $Pb(Zr,Ti)O_3$[7,10,12] and $(Pb,La)TiO_3$[23] Films

Recently, increased focus has been placed in processing ferroelectric $Pb(Ti,Zr)O_3$ (PZT) and $(Pb,La)TiO_3$ thin films. The processing of these thin films with desired perovskite structure has been required, because ferroelectric properties are influenced by the presence of a competing pyrochlore phase. The development of perovskite structure is more difficult in thin films integrated on substrates in comparison with the amorphous powders.

$Pb(Zr,Ti)O_3$ perovskite films have been successfully crystallized on various substrates such as MgO, $SrTiO_3$, and $Pt/Ti/SiO_2/Si$. Figure 3 summarizes the processing conditions of PZT thin films. The Zr and Ti ions located in B site of perovskite structure have to be coordinated in solution prior to the reaction with lead acetate anhydrate in order to form the perovskite films at low temperatures. Lead acetate anhydrate was selected because it is superior to other chemicals in effect to stabilize the precursor solution. The annealing of alkoxy-derived films in flow of water vapor and oxygen was found to be effective on the low temperature development and the preferred orientation of perovskite films. The films were crystallized into perovskite phase on $SrTiO_3$ substrate at 450°C.
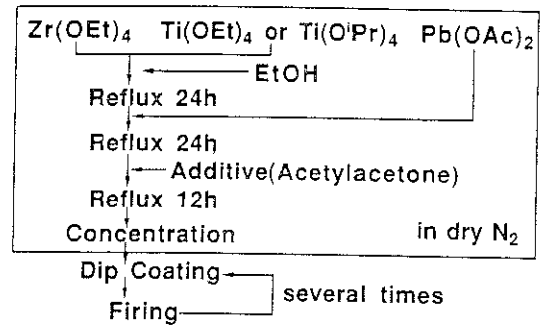

Fig.3 Scheme for processing of alkoxy-derived PZT films

Figure 4 shows XRD profiles of $Pb(Zr_{0.53}Ti_{0.47})O_3$ films on $Pt/Ti/SiO_2/Si$ substrate. The films, when properly crystallized, exhibit the typical ferroelectric hysteresis and a dielectric constant of about 500 at 100kHz at room temperature. Figure 5 summarizes the properties of the films crystallized at 600°C on passivated Si substrates. The permittivity increases from 50 to 500 with increasing thickness from 0.1 to 1.5 μm. The films have quite uniform and small grain size. The increase with film thickness corresponds to the increase in grain size of PZT.[10]
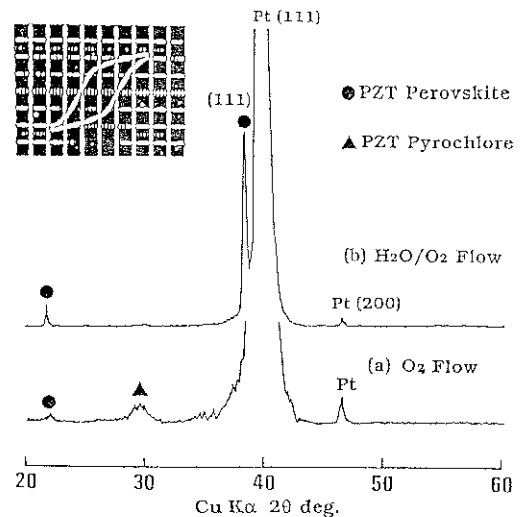

Fig.4 XRD profiles and D-E hysteresis curve of PZT (Zr:Ti=53:47) thin films on substrate ($Pt/Ti/SiO_2/Si$) crystallized at 600°C
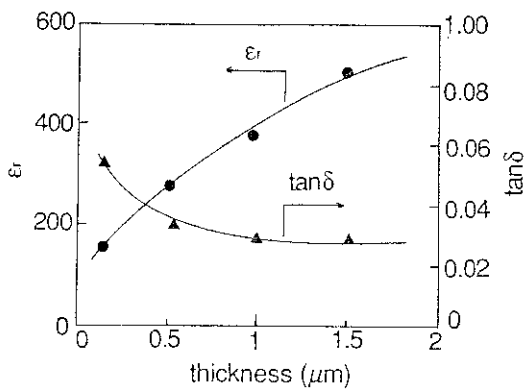
[Condition of calcinations: (a) O_2 flow (2) H_2O/O_2 flow]

Fig.5 Change of dielectric constant and tanδ at 100 kHz
for PZT films with film thickness

Lanthanum modified lead titanate ($Pb_{1-1.5x}La_xTiO_3$, PLT) has been receiving great attention for pyroelectric sensors, nonvolatile memories and large variety of electro-optic devices because of its excellent pyroelectric, ferroelectric and electro-optic properties. The properties of PLT can be controlled by the amount of lanthanum doping. Recently, the demand for thin film processing has increased for integrated-device development. (100) or (001) highly oriented PLT thin films are expected to give a large figure of merit and exhibit several excellent properties compared with other materials because of its polarization without poling treatment.

Highly oriented $Pb_{0.85}La_{0.1}TiO_3$ films were successfully synthesized on $LaNiO_3/SrTiO_3/MgO(100)$ substrates through metallo-organics. A homogeneous and stable PLT precursor solution was prepared from lead acetate, lanthanum isopropoxide and titanium ethoxide in ethanol. PLT precursor was stabilized by the coordination of acetylacetonate group to metals. Perovskite $Pb_{0.85}La_{0.1}TiO_3$ thin films with (100) or (001) preferred orientation were successfully synthesized on $LaNiO_3/SrTiO_3/MgO(100)$ substrates above 400°C. The orientation of the PLT film was improved markedly by using a $SrTiO_3$ thin film as a buffer layer between $LaNiO_3$ film and MgO substrate. PLT thin films on $LaNiO_3/SrTiO_3/MgO(100)$ substrates showed a typical P-E hysteresis. The dielectric constant of the film was about 600 at 25°C. The Curie temperature of the film was found to be at around 270°C.[23]

5. K(Ta,Nb)O3 (KTN) Films[12-14]

Potassium ethoxide, tantalum ethoxide and niobium ethoxide were used as starting materials. A certain amount ratio of tantalum ethoxide and niobium ethoxide was reacted in absolute ethanol to coordinate metal bondings in B-site of perovskite structure. Then a stoichiometric ratio of potassium ethoxide solution was added to react at refluxing temperature for 24 h.

The changes of coordination states in a KTN original precursor and partially hydrolyzed precursor were followed by NMR and FT-IR measurements. In the ^{13}C NMR spectra, bridging metal-oxygen bonds in the original precursor diminished to break-up, indicating that the condensation-polymerization reaction of metal alkoxides takes place. The behavior was also confirmed in FT-IR spectra.

An MgO (100) plate was chosen as a substrate because of the similar oxygen packing with KTN (100). XRD profiles of the KTN thin films crystallized at 675°C are shown in Fig.6. The formation of pyrochlore phase was observed after heat treatment without flow of water vapor (Fig.6(a)). A mixture of water vapor and oxygen gas during calcinations has a pronounced effect on the elimination of remaining organic components, leading to the formation of the preferred orientation of the perovskite phase (100) as shown in Fig.6(b), as observed in $LiNbO_3$ processing. Continuing the water vapor treatment hinders the further formation of the perovskite phase during the crystallization process, which might be attributable to potassium reacting with the hydroxy group and disturbing the network of the oxygen-metal bond at 675°C.

KTN65 (Ta/Nb = 65/35), KTN50 (Ta/Nb = 50/50), and KTN35 (Ta/Nb = 35/65) films were crystallized at 700°C on Pt(100)/MgO(100) substrates. The dielectric

measurements were conducted on 1.0-μm-thick KTN films. Figure 7 shows the variation in the dielectric constant as a function of temperature for the KTN50 film on Pt(100)/MgO(100) substrate. The maximum dielectric constant is observed at around 0°C at 1 kHz with a broad transition. The dielectric constant also depends upon the frequency. The transition range is shifted to higher temperature with increasing frequency from 1 kHz to 1 MHz. This result indicates a diffuse transition from a ferroelectric to a paraelectric phase. The broad peak is due to the stress in the films. Films having low stresses showed properties close to those of single crystals. However, films having large stresses showed broad peaks in the dielectric constant verses temperature curves with a diffuse phase transition.[14]
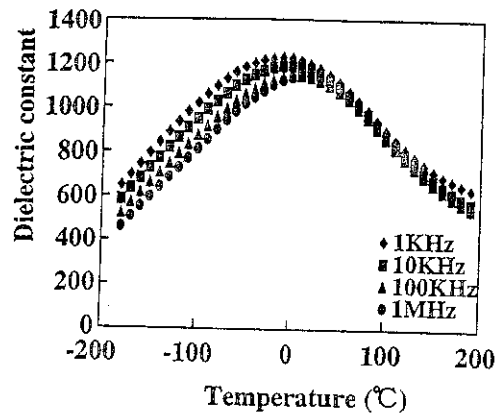
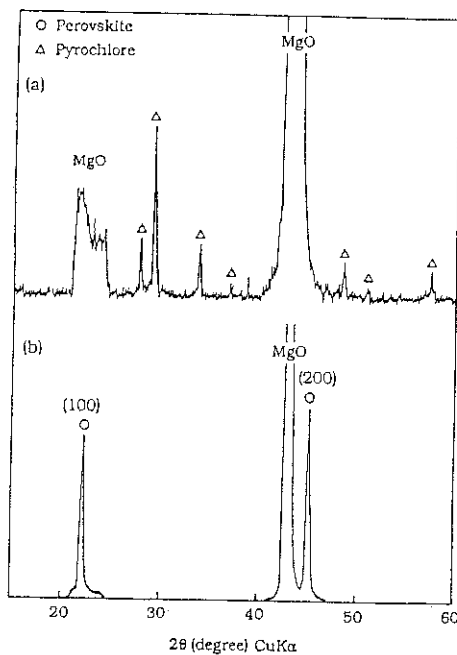Fig.7 Changes of dielectric constant for KTN50 films with temperature measured from 1 kHz to 1MHz

Fig.6 XRD profiles of $KTa_{0.65}Nb_{0.35}O_3$ thin films

on MgO(100) substrates crystallized at 675°C

after calcinations through (a) oxygen at 300°C and

(b) oxygen/water vapor at 300°C

6. Functional Fine Ceramic Particles/Polymer Hybrids

Inorganic/organic hybrids are expected to have novel features as well as the combined characters of each component. The conventional mixing of particles into organics usually causes the particle agglomeration due to the van der Waals force, leading to the degradation of the properties. The authors have developed a novel method to synthesize magnetic oxides or $BaTiO_3$ particles/organic hybrids through the reaction control of the designed precursor from modified titanium and barium alkoxide below 100°C.[15-18]

Tetragonal $PbTiO_3$ (PT) of perovskite structure is one of the ferroelectric and piezoelectric materials with attractive properties. Crystalline $PbTiO_3$ particles can be synthesized at 470°C from the precursor of lead acetate and titanium alkoxide. Usually, the heat treatment above 400°C is required to prepare crystallized $PbTiO_3$ particles. The authors discovered the crystallization of $PbTiO_3$ particles directly into perovskite phase below 100°C in organic matrix to form a hybrid.[19] Figure 8 shows the processing scheme for the preparation of hybrids. The fabrication of $PbTiO_3$/organic hybrids was carried out according to the scheme shown in Fig.9. Lead methacrylate and titanium

isopropoxide were weighed to be a molar ratio of 1.0 and dissolved in absolute methanol. The mixture was refluxed at 65°C for 24 h producing a clear PT precursor solution. The PT precursor is analyzed to comprise a complex alkoxide, $Pb[Ti(OR)_n(methacryl)]$. The solution was hydrolyzed with CO_2-free water, followed by the evaporation to afford a solid product, which was sealed with 2,2'-azobis (isobutyronitrile) (AIBN) and methanol under vacuum in a glass tube after freezing-melting treatments in order to remove oxygen and polymerized at 100°C. The solid hybrid was obtained after removal of solvent by drying under vacuumat room temperature.

diffraction and the Raman spectra of the oxide particles confirm to be crystalline tetragonal $PbTiO_3$ particles. The ratio of Pb to Ti was found to be 1:1 by the EDX analysis. The dielectric constant of a hybrid film, prepared from the $PbTiO_3$ precursor hydrolyzed with 30 equiv. water followed by polymerization at 100°C for 24h, is 5.2 at 10kHz at room temperature, which is higher than that of poly(methylmethacrylate) (PMMA) as the matrix. The hybrid in silicone oil suspension behave as the typical electrorheological fluid as shown in Fig.10, which affords a novel modified ceramic material in the emerging areas.
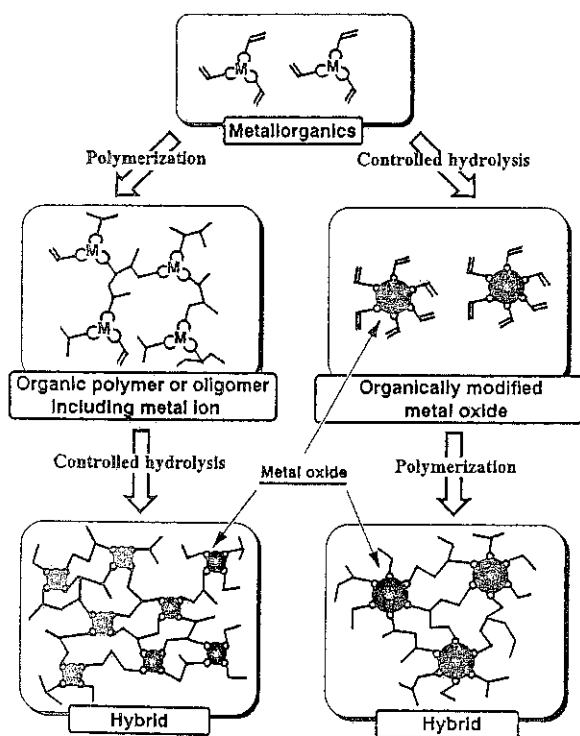

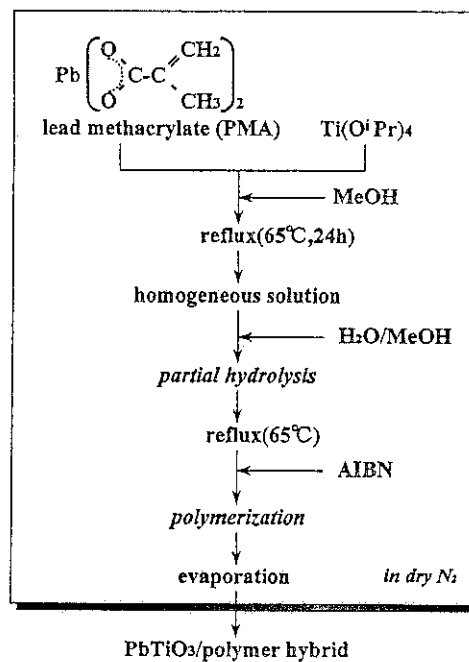Fig.8 Chemical processing scheme of hybrids

Fig.9 Processing of PbTiO₃/polymer hybrid

The hybrid films were prepared from the hybrid powder by pressing between electrically heated planes at about 170°C. Crystalline perovskite $PbTiO_3$ particles/organic hybrids behave to be dielectric and respond to the applied electric field as an electrorheological fluid. The selected area electron
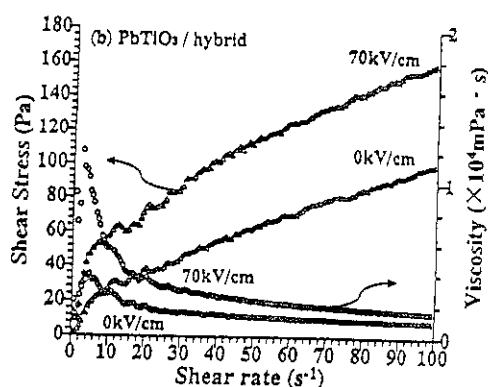
Fig.10 Shear stress and viscosity changes
as a function of shear rate on PbTiO₃/hybrid

7. Conclusions

The concept described in this paper can be applied to the processing of functional ceramics with controlled characters and orientations at relatively low temperatures. The crystallization of films can be promoted by the reaction control of designed metal alkoxides in intermediate state and then the pre-heat treatment of alkoxy-derived films in flow of water vapor and oxygen gas mixture. The chemical processing does realize a promising route to synthesize functional ceramic films, which leads to the integration of functionalities.

The newly developed method provides novel inorganic/organic hybrids below 100°C through the reaction control of designed metallo-organic molecules with combination of the polymerization, which creates the future strategy of the new material families.

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