MISSOURI S&T

Missouri University of Science and Technology

Scholars' Mine

Materials Science and Engineering Faculty Research & Creative Works

Materials Science and Engineering

01 Jan 1994

Processing and Characterization of Samarium and Manganese Modified Lead Titanate Thin Film

Chen-Lung Fan

Wayne Huebner
Missouri University of Science and Technology, huebner@mst.edu

Follow this and additional works at: https://scholarsmine.mst.edu/matsci_eng_facwork

Part of the Materials Science and Engineering Commons

Recommended Citation

PROCESSING AND CHARACTERIZATION OF SAMARIUM AND MANGANESE MODIFIED LEAD TITANATE THIN FILM

Chen-Lung Fan and Wayne Huebner
University of Missouri-Rolla, Rolla, MO 65401

ABSTRACT

Samarium and manganese modified lead titanate thin films were fabricated by spin-coating an amorphous citrate precursor. These films transformed into an oxide film upon heat treatment at 400°C or above. Relatively large area and crack-free thin films could be obtained by this process both easily and inexpensively. The rheological behavior of the precursor solution, as well as its thermal decomposition and phase development were studied by means of DSC/TGA and XRD. The thickness and grain size of the oxide film were examined by TEM and SEM. .

INTRODUCTION

Lead titanate $PbTiO_3$ (PT) exhibits many intriguing features such as a high Curie Temperature ($T_C \approx 490°C$), large k_t to k_p ratio, and a large pyroelectric coefficient, which qualifies it to be one of the candidates suitable for making acoustic transducers or pyroelectric detector [1]. Due to its large c/a ratio, however, it cannot be sintered to high density without falling apart when it cools through T_C. To overcome this drawback and still maintain its interesting properties, it has to be doped to lower the c/a ratio [2]. Among these effective dopants, Sm^{3+} and Ca^{2+}–doped PT are two major systems which demonstrate superior properties [3, 4]. In this study PT doped with 10 mol% Sm^{3+} and 2 mol% Mn^{2+} was chosen as the compositional system to work with.

The purpose of this study was to synthesize Sm^{3+} and Mn^{2+} modified PT thin films by spin coating of amorphous citrate precursor on various substrates. Compared with chemical vapor deposition (CVD) [5, 6], physical vapor deposition (PVD), and relatively inexpensive sol-gel process [7, 8], the process used in this study is even more inexpensive. It also offers the advantage of easier control of the chemical stoichiometry and of having a variety of selections of starting materials. Generally all water soluble metal salts can be the starting materials provided that the metal salts are compatible with one another, unlike CVD and sol-gel processes which require few available and expensive precursors. The problems associated with the amorphous citrate process lie on the requirement of heat treatment at 400°C or above in order to convert the precursor resin into oxide thin film. Therefore care has to be taken on controlling the precursor film thickness to ensure a crack-free thin oxide film is to be obtained after heat treatment. In addition, selection of a substrate material with a compatible thermal expansion coefficient is also very important to the perfection of the thin film. Those problems and concerns will be discussed in the following sections.

EXPERIMENTAL PROCEDURE

Titanium isopropoxide, lead carbonate, samarium carbonate, manganese acetate, and citric acid were used as the starting materials. The process, as shown in the flow chart of Fig. 1, starts with a titanium citrate complex solution, since titanium isopropoxide is not water soluble and is subject to hydrolysis. Citric acid was first dissolved in distilled water with a pH value of ≈ one, followed by the addition of ammonium hydroxide until the pH value reaches six (solution A). On the other hand, titanium isopropoxide was diluted with isopropyl alcohol to 50 vol.% (solution B). Solutions A and B were mixed and heated on a hot plate. Upon mixing, titanium isopropoxide underwent a fast hydrolysis reaction, forming titanium hydroxide which was then gradually dissolved into the solution. The solution thus made can be concentrated by boiling off more water in the solution, and can be stored indefinitely in a liquid form without forming precipitates. It can also be further concentrated and vacuum dried into a crystallized form, as confirmed by XRD. In this study, it was kept in the solution form and standardized gravimetrically to determine the specific amount of titanium ions in the solution. Lead carbonate, samarium carbonate, and manganese acetate were also standardized to achieve better control over the stoichiometry of the final thin oxide film.

The desired amount of titanium solution was heated on a hot plate until the temperature reached 100°C, then a suitable amount of lead carbonate, samarium carbonate, and manganese acetate were added into the solution to prepare the precursor for the oxide composition of $(Pb_{0.9} Sm_{0.1})(Ti_{0.98} Mn_{0.02})O_3$. Carbon dioxide was released when the carbonates reacted with titanium citrate solution, and all the cations were chelated with citric acid forming a citrate complex. The complex solution was then oven-dried at 100°C until all the water was driven off leaving a pile of cracked-up resin powders which can be redissolved into water to make up solutions with different concentrations. Especially for the preparation of spin-coating precursor solution, it is necessary to know the concentration of the solution so that the process can be easily controlled. Otherwise, the concentration of the solution will depend on how much water remains in the solution, which is very difficult to control and to reproduce since water is vaporizing all the time during the preparation of the citrate complex solution at temperature as high as 100°C. The resin powders were then collected for DSC/TGA studies and for the preparation of the precursor solution for spin coating.

The rheological behavior of the precursor solutions with different concentrations was characterized by a HAAKE viscometer.

Spin coating was carried out by a computerized spin coater which has the ability to controlling acceleration and soak time. Generally speaking, higher solution concentration gives rise to thicker coating layer and higher spin speed favors lower coating thickness. Therefore it is really a matter of compromising the solution concentration and the spin speed in order to obtain an optimum coating thickness, which allows the formation of a uniform and crack-free thin oxide film after heat treatment. In this study, 20wt.% as the solution concentration and 0 rpm up to 2000 rpm in 30 seconds as the acceleration schedule was chosen to prepare the thin films for all the studies.

After the precursor solution was coated on to a silicon wafer or polished kovar substrate, it was heat treated at 400°C for 10 minutes in a Linberg box furnace for all the organic species to be oxidized, leaving behind a uniform thin oxide film. Multiple coatings could be done by repeating the procedures to build up the thickness. The measurement of film thickness was performed by SEM and the grain size of the film was illustrated by TEM.

RESULTS & DISCUSSION

The oven dried resin, unlike the room temperature vacuum-dried resin, appeared to be x-ray amorphous and exhibited a yellowish color. To characterize the rheological behavior of the precursor solution, shear stress as a function of shear rate was measured on the solutions with different concentrations. Fig. 2 shows this behavior for 20, 40, 50, and 60 wt.% of the precursor solutions. Although the sets of data are somewhat fluctuating, they still show a linear trend of the shear stress as a function of the shear rate and there is no yield stress associated with them. This qualifies the solution with concentration of 60 wt.% or below as a Newtonian solution. The corresponding average viscosities are 3, 5, 10, and 50 mPas for 20, 40, 50, and 60 wt.%, respectively. Compared with that of water, which is about 1 mPas, the viscosities are still on the low. As the concentration increases further, the viscosity increases drastically (Fig. 3). At 75wt.% the viscosity is 37,000 mPas, which is about 750 times that of the 60 wt.% solution.

Normally it is required to have medium viscosity (100-1000 mPas) for the spin coating process to be successful, provided that the viscosity does not change during the coating process. If the precursor solution has too low viscosity, there will no solution coated on the substrate after the spinning process since all the solution is spun away. However, if the solution viscosity is too high, the coating layer will not be very uniform and probably too thick to obtain a crack-free thin oxide film. Note that the coating thickness results from the combining result of the solution concentration and the spinning speed. Therefore, for low
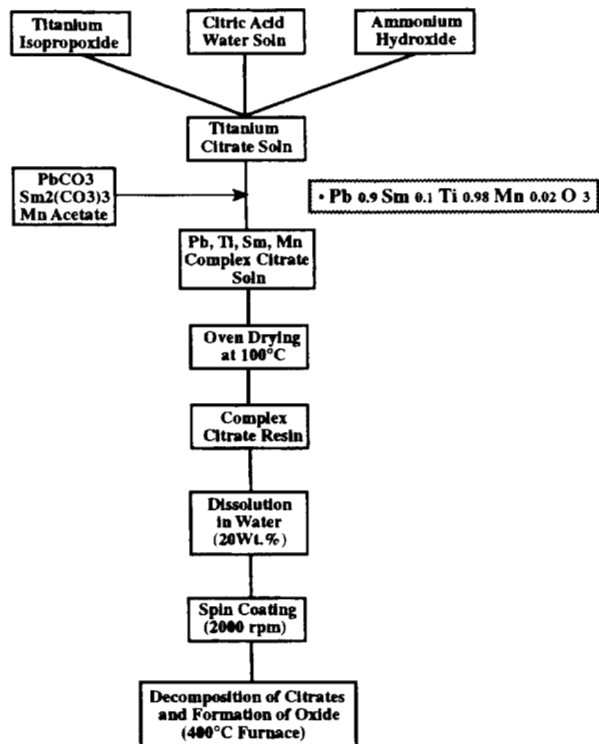
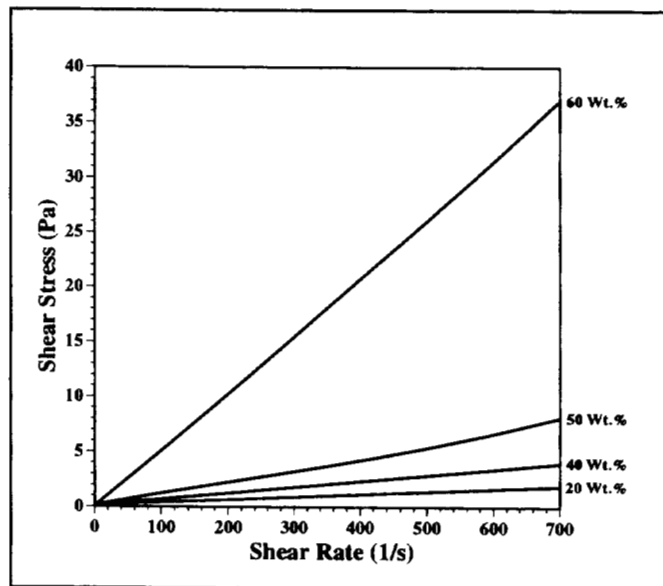Figure 1.   Flow chart of the experimental procedures.

concentration, say 20wt.%, low spin speed will be favorable, and for high concentration, say 70wt.%, high spin speed is favorable, assuming that the viscosity does not change as the process goes on. Unfortunately, the viscosity of the solution increases as the spinning process goes mainly due to the loss of water content, which results in increase of solution concentration and in turn increase of the viscosity. As can be seen in Fig. 3, when the solution concentration increases to above 70 wt.% the viscosity increases hundreds of times of that of the 20 wt.% solution. Therefore it is not difficult to understand that 20 wt.% solution can be spin-coated on a substrate, thereby forming a thin layer of precursor resin. The 20 wt.% solution keeps drying out as the process goes, while some of the excess solution is spun away when the viscosity of the solution is still low enough to allow that to happen.

After the precursor resin is spin-coated, heat treatment converts the resin film to an oxide film. Soon after a substrate is inserted into a Linberg box furnace, the resin film starts turning brown and black due to the charring of the resin and then the color goes away about five to ten minutes after the substrates being inserted into the furnace. These colorless thin films are transparent to visible light, which indicates the good uniformity of the thin films. Basically this process can be applied to any substrate which is thermally durable such as glass, silicon wafer, and stainless steel. To meet the requirements of different purposes, substrates have to be selected properly. For example, glass substrates can be selected for optical application, silicon wafer for TEM study, and stainless steel for electroceramic application since the substrate is not only a substrate but also a conductive electrode. In this study, silicon wafer was used as the substrate to prepare TEM specimen and kovar, a low thermal expansion alloy, was used as the substrate for grain growth studies mainly because of its low thermal expansion coefficient. This allows the thin film to adhere to the substrate tightly without being debonded due to thermal expansion mismatch at temperatures higher than 400°C.

Fig. 4 shows the DSC/TGA study on the oven-dried resin. (5°C/min. up to 1000°C). It can be seen that the resin starts decomposing at $\approx$ 200°C judging from the exotherm and accompanying weight loss, and it finishes decomposing before 500°C. At temperature higher than 500°C there is no exotherm or weight loss. The final product of the experiment was determined as perovskite PT powders by XRD.
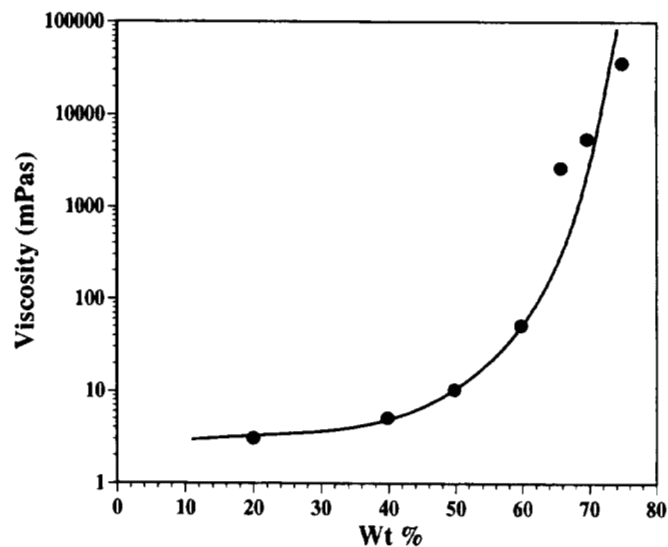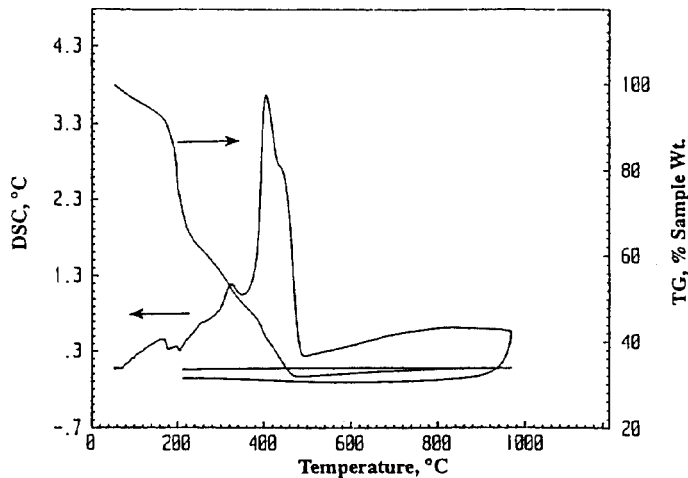

Figure 2.   Shear stress as a function of shear rate for precursor solution with different concentrations.

Figure 3.   Viscosity as a function of solution concentration.

513

Figure 4. DSC/TGA versus temperature for the oven dried precursor resin.

PbTiO3, tetragonal, JCPDS # 6-0452

Figure 5. X-ray diffraction patterns at different temperatures of the PT thin films on kovar substrates.

Presumably the decomposition temperature of the bulk resin should be the same as the thin resin film on the substrates, however, there are some slight differences between them. In the case of the DSC/TGA study, the resin powders were put in an Al_2O_3 crucible. And it is foreseeable that those powders near the surface will experience thermal radiation from the furnace more directly than those near the bottom of the crucible. Perhaps even more importantly those powders on the surface are experiencing higher oxygen partial pressure than those in the interior. Therefore the decomposition behavior of the resin is indeed an overall result of a kinetic process, and it may not reflect the real decomposition temperature. But it is still safe to say that the resin decomposes in the temperature range from 200°C to about 500°C. On the other hand, thermal decomposition of the resin films on substrates would be more uniform since the film is so thin that the temperature or pO_2 gradient between the top and bottom surface is negligibly small.

Fig. 5 shows the x-ray diffraction patterns for the kovar substrate and for the modified lead titanate thin films on kovar which has been heat treated at 400, 500, 600, and 800°C for 30 minutes. As can be seen from the figure, the thin films have crystallized at temperature as low as 400°C. And there is no black carbon residue found visually on the film treated at 400°C, which confirms that the resin films can be fully converted to crystallized oxide films at this temperature. Compared with the DSC/TGA data, which shows a wide temperature range from 200 to 500°C, it clearly shows that the decomposition temperature suggested by the DSC/TGA study is a result of an overall kinetic process. As the films were treated at higher temperatures, the diffraction peaks became sharper and narrower, which indicates the crystal size is increasing. When the temperature gets up to 800°C, the tetragonal splitting of the peaks corresponding to (001) and (100) planes can be clearly seen. This confirms that the crystal structure of the film is tetragonal phase and the reason that the diffraction patterns for below 800°C show cubic like structure is due to line broadening caused by the small crystal size of the film.

Another interesting observation regarding the diffraction patterns in Fig. 5 is that the crystals in the film exhibit a preferred orientation. According to the standard powder diffraction file for tetragonal PT (JCPDS file # 6-0452), the relative peak heights correspond to (001), (100), (101), (110), and (111) planes are 25, 50, 100, 55, and 40, respectively. However, the peak heights for the thin film show different relative intensities, namely 100, 87, 100, 6 and 32, respectively, as compared in Table I. Clearly the peak intensities of (001) and (100) planes for the thin film are significantly higher than that for the powder diffraction file. Also the (001) peak intensity is higher than the (100) peak intensity unlike the powder diffraction file of which the (001) peak intensity is only half the (100) peak intensity. Another feature regarding the change in peak intensity is that (110) peak intensity for the thin film almost diminishes, relative peak intensity of 6, as compared with that of 55 for the powder diffraction file. All these observations indicate that the film is somewhat preferred oriented along [001] direction.
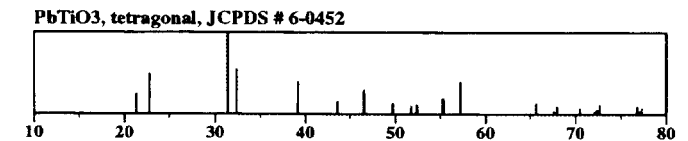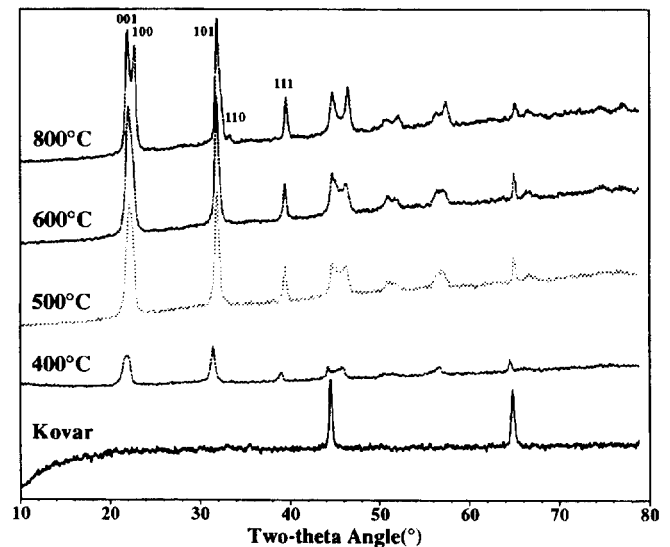
It is known that pure PT has a $T_C \approx 490°C$. For the Sm^{3+} and Mn^{2+} doped PT composition used in this study, the $T_C \approx 350$ °C due to the lower c/a ratio There are two possibilities for the preferred orientation: one is that the atoms in the film aligned themselves along the crystal direction of the substrate thus forming preferred oriented crystals, provided that the lattice mismatch between the film and the substrate is not too much; the other one is that the crystals align themselves along c direction during phase transformation from cubic to tetragonal phase. Since the kovar substrate used in this study is not even a single crystal material, it is unlikely for the crystals in the film to grow on the substrate along a specific direction. Therefore the preferred orientation of the crystals in the thin film on kovar is believed to form during phase transformation. For thin films on substrates, there is only one free direction for the crystals in the film to either expand or to shrink because the dimensions of the substrate is constant which gives rise to a constraint stress along the substrate plane. In other words, the films on the substrates are two-dimensionally constrained, and if there will be any dimension change, while still remain the integrity of the films, it has to be happening along the normal direction of the substrate.

For PT to transform from the cubic to the tetragonal phase, it does not require atomic rearrangement and can be done simply by expanding in c direction and shrinking in a direction. Considering the peak intensity data shown in Table I, there are indeed more crystals whose c axes are perpendicular to the substrate since the peak intensity of (001) plane is much higher than what would be expected if all the crystals are randomly oriented. In mind with all the aforementioned arguments, it confirms that the preferred orientation of the crystals in the thin film is a result of reorientation of the crystals which happens during phase transformation from cubic to tetragonal phase.

Table I. Comparison of peak heights of x-ray diffraction patterns of PT thin film and that of JCPDS file # 6-0452.

(h, k, l)	001	100	101	110	111
Intensity JCPDS # 6-0452	25	50	100	55	40
Intensity PT film	100	87	100	6	32

514

Fig. 6 shows the TEM micrograph of the lead titanate thin film after being stripped off the silicon wafer. The coating process was exactly the same as that used for coating on kovar. After the silicon wafer was coated with a layer of precursor resin, it was first treated at 400°C to convert the resin into oxide thin film, and then it was immersed into a 10wt.% sodium hydroxide water solution preheated at 80°C. Soon after the immersion, sodium hydroxide started reacting with the silicon wafer, and the thin film was stripped off the substrate as soon as the bonding between the film and the substrate was destroyed. The stripped film was then transported into a 250 ml beaker which contains 200 ml of water solution, 98 vol.% of water and 2 vol.% of methanol, to wash away the residual sodium hydroxide on the film. Then the film was lifted and supported on a copper grid for TEM study. According to Fig. 5, the grain size was estimated ranging from less than 10 nm to a few tens nm, though the film contains a few layer of grains which makes the measurement of grain size more difficult.
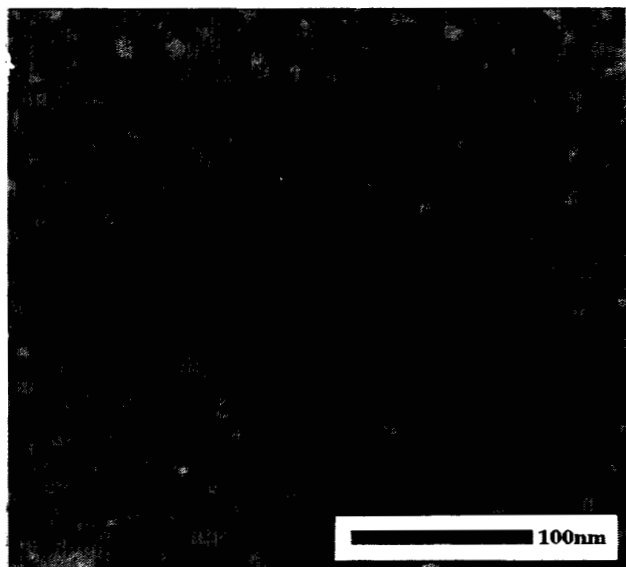

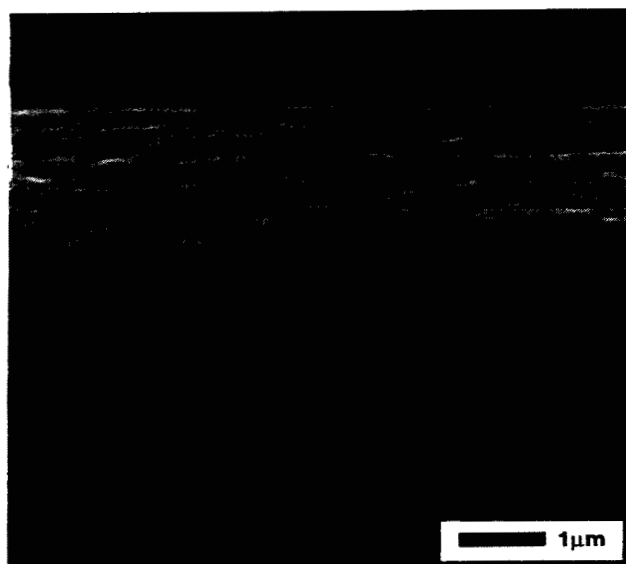Figure 6.   TEM micrograph of the PT thin film stripped off the silicon wafer.

Figure 7.   SEM micrograph of the PT thin film on kovar substrate.

Fig. 7 shows the SEM micrograph of the cross section of lead titanate thin film coated on kovar and heated at 800°C. The sample was first mounted with epoxy and then ground with a 600 grit paper followed by polishing with 0.3 μm alumina polishing media. The film thickness is about 2.3 μm after 40 coatings. Therefore the average thickness of a single coat is about 0.06 μm. Although it is a little troublesome to coat forty times in order to build up 2.3 μm layer of film, it was demonstrated useful in coating on glass substrates for optical application, which does not necessarily require film thickness of more than 1 μm.

CONCLUSIONS

Samarium and manganese modified lead titanate thin films were successfully fabricated by first spin coating a layer of amorphous citrate precursor resin on glass, silicon wafer, and kovar substrates, followed by heat treatment at 400°C to convert the resin film to oxide film. X-ray result shows that perovskite phase was obtained after the heat treatment and also the crystals in the film were preferred oriented mainly along [001]. The grain size of the film treated at 400°C ranges from less than 10 nm to a few tens nm as indicated by the TEM micrograph. The average film thickness for a single coat is about 0.06 μm, which is very suitable for optical applications rather than dielectric or piezoelectric applications. Therefore more work will be concentrated on optical application of films made by this process. In addition, grain growth of a free standing film, also made by this process, is currently undergoing in the authors' group and will be published soon.

REFERENCES

[1]   Laurel M. Sheppard, Advances in Processing of Ferroelectric Thin Films, *Am. Cer. Soc. Bull.*, Vol. 71, No. 1, 1992.
[2]   A. Ahmad et al, Processing and Characterization of Ca, Ce, and Na Ion Doped Lead Titanates, *Proc. of the Eighth International Symposium on Application of Ferroelectrics*, IEEE, New York (1992).
[3]   Takashi Takahashi, Lead Titanate Ceramics with Large Piezoelectric Anisotropy and Their Applications, *Am. Cer. Soc. Bull.*, Vol. 69, No. 4, 1990.
[4]   Thitima Suwannasiri and Ahmad Safari, Effect of Rare-Earth Additives on Electromechanical Properties of Modified Lead Titanate Ceramics, *J. Am. Cer. Soc.*, 76 [12] 3155-58 (1993).
[5]   Kwang Ho Kim et al, Effect of Antimony Addition on Electrical and Optical Properties of Tin Oxide Film, *J. Am. Cer. Soc.*, 77 [4] 915-21 (1994).
[6]   Toshiro Maruyama and Susumu Arai, Electrochromic Properties of Tungsten Trioxide Thin Films Prepared by Chemical Vapor Deposition, *J. Electrochem. Soc.*, Vol. 141, No. 4, April 1994.
[7]   Charles D.E. Lakeman and David Payne, Processing Effects in the Sol-Gel Preparation of PZT Dried Gels, Powders, and Ferroelectric Thin Layers, *J. Am. Cer. Soc.*, 75 [11] 3091-96 (1992).
8.   Debtosh Kundu et al, Preparation and Optical Property of Sol-Gel-Derived Cu-SiO$_2$ Thin Films, *J. Am. Cer. Soc.*, 77 [4] 1110-12 (1994).