Journal of the European Ceramic Society 21 (2001) 1557–1560

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Structural observation of PZT system film in the use of pulsed-laser deposition method

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Received 4 September 2000; received in revised form 2 November 2000; accepted 15 November 2000

Abstract

This paper reports the structural observation of the lead zirconate titanate system formed in the pulsed laser deposition method. Scanning electron microscopy and X-ray diffraction was used for surface and the crystal structure observation. The target materials are prepared in the conventional solid state reaction method in oxide powder. Perovskite structure was formed on the magnesium oxide substrate. On the other hand, this is not the case on the silicon substrate, which has a pyrochiore or amorphous and relatively void structure. This shows that the film formation behavior depends on not only the formation condition, e.g. temperature, vacuum ratio etc., but also on the substrate material.

Keywords: Electron microscopy; Films; PLZT; PZT; X-ray methods

1. Introduction

There has been developing many micro fabrication technologies, including film formation, structure and system integration. Ferroelectrics is one of the promising materials, which have piezoelectric and pyroelectric properties and is applicable to many micro electrical devices. It is necessary to develop and establish a new energy transfer method in order to supply energy to micro electromechanical systems (MEMS) and micro opto-electromechanical systems (MOEMS) in the near future.[1] In particular, the wireless telecommunication or energy transfer method has been paid much attention.[2] One of the reasons for this condition is that it is difficult to disregard the weight of devices and the friction of the wire in MEMS. It is, therefore, useful to apply photovoltaic materials, e.g. some lead zirconate titanate (PZT) system including lead lanthanum zirconate titanate (PLZT), to power transducer of micro electrical devices.

Lead lanthanum zirconate titanate, which is $Pb_{1-x}La_x(Zr_yTi_z)_{1-x/4}O_3$ abbreviated as PLZT or PLZT($X/Y/Z$), where $X = 100\,x$, $Y = 100\,y$ and $Z = 100\,z$, is a ferroelectric solid solution that has wide-ranging material properties which depend on its composition. Some compositions of PLZT are applicable for various kinds of electro-optical devices. Haertling and Land first developed this material as a ferroelectric transparent ceramics.[3] PLZT has at least five phases at room temperature: two ferroelectric phases, intermediate, anti-ferroelectric, and paraelectric phase.

Among them PLZT(3/52/48), which underlies the phase boundary between I and II, has photostrictive properties. This phenomenon is the superposition of photovoltaic[4] and inverse piezoelectric effect. Photostrictive effect is caused by light illumination in the near ultraviolet region. These materials can be used in micro-devices to directly convert optical energy to mechanical energy, which is firstly proposed as opto-mechanical actuators.[5] This property is useful for the energy conversion in the micro electro-mechanical system (MEMS) and photo acoustic devices.[6] Some of the researches have been already reported in practical[6,7] and scientific[8,9] points of view.

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0955-2219/01/$ - see front matter
PII: S0955-2219(01)00063-2

Pulsed-laser deposition (PLD) formation process has been used in various kinds of thin film devices,[10,11] in order to obtain high-quality ferroelectric materials. PLD has some advantages in the following,[12] i.e. (1) low temperature formation compared with MOCVD and electron beam deposition, (2) the straight direction of plume movement, and (3) the suitable adjustment with the semiconductor production system. This is suitable character in application to the LSI process, where it is afraid to cause of the heat damage and heat diffusion.

This paper will show, preliminarily, the process of the PLD on some PZT materials and also the structural observation of formed films. X-ray diffraction and scanning electron microscopy (SEM) were carried out in this obseivation.[13,14] The film formation behavior is different in the case of Si and MgO substrates in spite of the same deposition condition. Substrate effect to the film growth plays an important role in PLD technology.

2. Sample preparation and experimental set-up

2.1. Target preparation

Target materials are used in the conventional solid state reaction method.[8,15] The preparation procedure has been reported elsewhere more detail.[16] Raw materials are lead oxide (PbO), zirconium oxide (ZrO_2), titanium dioxide (TiO_2) in the case of PZT. These powders are weighed preciously. The prepared powder is arranged to be just the same of its stoichometric composition. Excess PbO addition is not carried out in this target production process. The purity of all raw powders is 99.99% and these particle sizes are under 50 μm (300 mesh). The mixing process is carried out in wet ball milling with ethanol. Tungsten oxide (WO_3) was used as the additive in order to enhance the photovoltaic properties of PLZT. The quantity of WO_3 is 1 wt.% of the total weight of the mixture. Pressed powder was sintered in the air at 1200°C for 2 h. The resulting block was cut into approximately 20 mm in diameter and 3 mm thick.

Material characteristics of the prepared targets are estimated shown in the following sections. The density of the samples is measured in use of the Archimedes method. Crystal structure of the sample is measured in use of X-ray diffraction apparatus (Rigaku Miniflex) in $\theta-2\theta$ method. The surface observation is carried out in use of the scanning electron microscope. Before the SEM observation, carbon coating was carried out in use of the vacuum coater. The acceleration voltage of SEM was 7 kV.

2.2. Experimental apparatus of PLD method

The experimental set-up is shown in Fig. 1 and the deposition condition is shown in Table 1. The apparatus consists of the laser system, the optical system and the thin film formation chamber. The deposition chamber has a rotating target holder. This holder can revolve round the laser line axis while rotating in its own axis. The rotation of the substrate is effective to the homogeneous film formation. The substrate heating system is also equipped in the deposition chamber. The ArF excimer laser light illuminates the rotating target materials through the focusing optical system. The plume produced from the target moves toward the substrate and makes formation of the thin films on the substrate. The vacuum system has rotary and turbo molecular pump in order to reach the 10^{-7} Torr at room temperature.

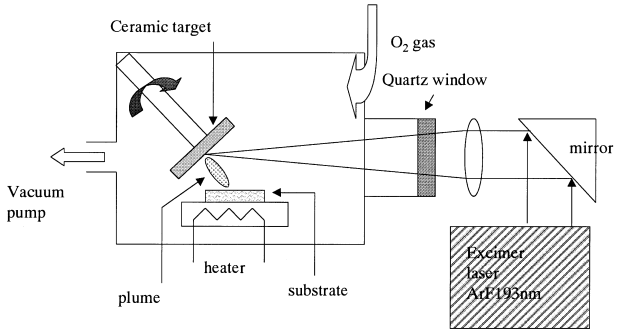

Fig. 1. Schematic figure of the pulsed laser deposition apparatus.

Table 1
Experimental conditions of the PLD

Target	PLZT(3/52/48)+ 10% PbO, PZT(52/48)
Substrate	MgO(100), Pt/Ti/$Si0_2$/Si
Substrate heating	500°C
Gas	O_2
Gas pressure	0.01∼0.5 Torr
Laser	ArF excimer (193 mu)
Frequency	5 Hz
Beam size	0.3 cm^2
Deposition time	60 min
Target-substrate distance	20 mm
Laser beam fluence	5.6 J/cm^2

MgO and Pt/Ti/Si substrates and PZT and PLZT targets are prepared in this time. MgO substrate without electrodes has high resistance which is suitable to electrical insulation between film and substrate. The vacuum condition of the chamber is 100 mTorr. The laser pulse energy was 100 mJ. The laser output pulse repetition rate is 5 Hz. Laser beam fluence is 5.6 J/cm^2. In the heating system, the substrate holder reached 500°C in 3 h. Rapid thermal annealing is not used in this apparatus.

3. Results and discussion

3.1. Experimental results

Table 2 is a summary of experimental results. In both cases of sample 1 and sample 2, a 200 nm thick thin film was obtained. Heating temperature during the deposi-

Table 2
Characteristics of the formed films in PLD method

Target	Substrate	Structure	Note
PLZT(3/52/48) + 10% PbO (Sample 1)	MgO(100)	Perovskite	Substrate heating
PZT(52/48) (Sample 2)	Pt,Ti/SiO_2/Si	Pyrochlore, amorphous (total structure)	Substrate heating

tion is 500°C. The obtained film has a slight thickness slope in accordance with the distance from the plume, and the film has color stripes. Fig. 2 shows the SEM observation picture of the surface of film. The surface has a homogeneous structure. Fig. 2(a) is the case of PLZT-target and MgO-substrate. Fig. 2(b) is the case of PZT-target and Si-substrate. The surface of the film is leaned around 6° to the horizontal plane for the release of the charge-up. Fig. 2(a) shows film surface, where has the homogeneous and small particle. The average size of the particle is around 100 nm. On the other hand, this is not the case in Fig. 2(b). The surface has a relative void structure compared with Fig. 2(b). Fig. 3 shows XRD pattern of the (a) PLZT and (b) PZT. Since the peak of (100) reflection around $2\theta = 22°$ is shown, the perovskite structure is formed in case of the PLZT [Fig. 3(a)]. But this reflection is not shown in Fig. 2(b).

In case of the Si substrate, almost the same film is obtained in thickness. Substrate heating condition is also the same. The perovskite structure is not formed in this film in spite of the same formation condition. The surface structure of the film has totally different surface structure compared with the MgO substrate through the SEM observation.

3.2. Discussion

Sample 1 has a totally perovskite structure with orientation to (001) directions in the film surface. In case of sample 1, the target is sintered and the substrate heating temperature is about 500°C. Sintered target and substrate heating in PLD is important to form the perovskite structure. Sintered target is useful not to release of the impurity materials and gas form the target. The chamber vacuum condition became bad in use of the non-sintered target. Perovskite structure is also not obtained without substrate heating.

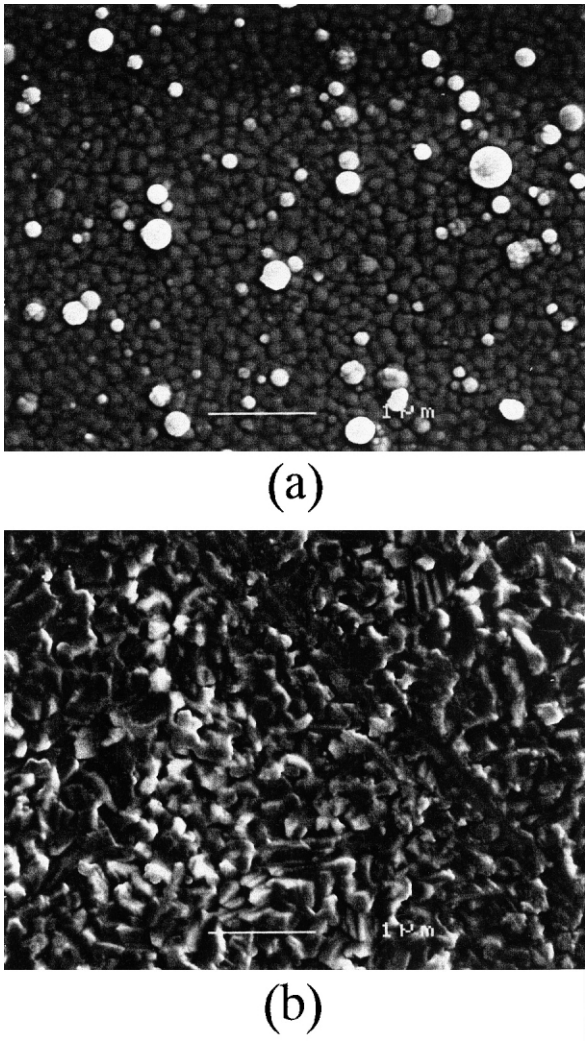

Fig. 2. SEM observation of the formed films. (a) PLZT on MgO and (b) PZT on Si.

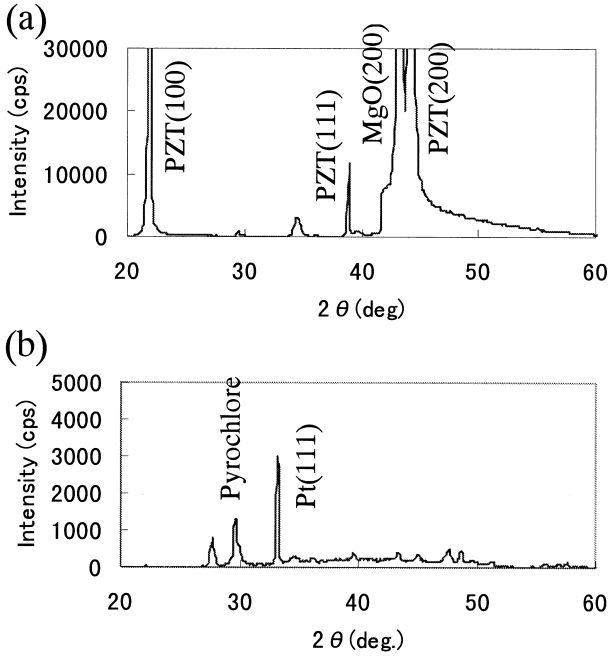

Fig. 3. X-ray diffraction patterns of the formed films. (a) PLZT on MgO and (b) PZT on Si.

In spite of the same experimental conditions of sample 1, the same crystal structure is not obtained in case of sample 2. The surface of sample 2 has relatively spare structure compared with the MgO substrate case. These differences are due to the substrate materials. So-called 'substrate effect' to the film formation is frequently reported. This could be originated from the lattice matching or the heat conditions including conductivity and differences of the thermal expansion coefficients between the substrate and the films. The evaporated target materials of PLZT and PZT are condensed at the surface of the substrate. Heating power of the substrate holder almost so high that temperature is kept constant during the deposition.

It is necessary for the formation of the perovskite structure to use the PbO excess target (e.g. PZT(52/48) + 10 wt.% PbO). Some volume of the Pb element is evaporated in the calcined and sintered process. The excess PbO target is so suitable as to compensate the evaporation Pb during the heating process. The same condition has been already reported in another process techniques.[17]

Even though the systematic comparison of same material and substrate and the most suitable experimental conditions have not yet been fully clarified, the sintered target and the enough substrate heating are necessary to obtain the perovskite structure.

4. Summary

The thin film formation of PLZT and PZT with 200 am in thickness was carried out. The structure of the film was observed in use of the XRD and SEM. The substrate effect on the film structure is shown in this case. MgO substrate could play important role in the growth of the perovskite structure. But Si substrate is not suitable to grow the perovskite structure in this condition. PbO excess addition to the target is also effective to the structure formation. The mechanisms of this effect have not fully clarified yet but the lattice matching and the heating temperature is the key parameter of PLD formation.

Acknowledgements

We express our thanks to Ms. K. Saito for her technical co-operation in the scanning electron microscopy observation. We also thank Dr. K. Ozaki (Mechanical Engineering Laboratory) for useful discussions. Target preparation was carried out in co-operation with Mr. A. Yoshida (Furuuchi Chemical Corp.) and X-ray analyses with the Rigaku Co. Ltd. We thank Dr. S. Kokaji and Dr. T. Kojima (Mechanical Engineering Laboratory) for their encouragement of this work.

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