Annealing Effects of Laser Ablated PZT Films

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Abstract

Deposition of PZT with UV laser ablatio was applied for realization of thin film sensors and actuators. Deposition rate of more than 20nm/min was attained by pulsed KrF excimer laser deposition, which is fairly better than those obtained by the other methods. Perovskite phase was obtained at room temperature deposition with Fast Atom Beam(FAB) treatment and annealing.
Smart MEMS(Micro electro-mechanical system) is now a suject of interest in the field of micro optical devices, micro pumps, AFM cantilever devices etc. It can be fabricated by deposition of PZT thin films and micromachining. PZT films of more than 1 micron thickness is difficult to obtain by conventional methods. This is the reason why we applied excimer laser ablation for thin film deposition. The remanent polarization Pr of 700nm PZT thin film was measured, and the relative dielectric constant was determined to about 900 and the dielectric loss tangent was also measured to be about 0.04. XRD analysis shows that, after annealing at 650 degrees C in 1 hour, the perovskite structure would be formed with some amount of pyrochlore phase, as is the case of the annealing at 750 degrees C in 1 hour.

Key Words : PZT, MEMS, PLAD, annealing, thin film

1. Introduction

The solid solution system $Pb(Zr,Ti)O_3$ (PZT) is one of the best known ferroelectric ceramics that have the perovskite structure(Fig. 1). Its phase diagram is shown in Fig. 2(1). In this diagram, one can easily see at around Zr:Ti=1:1 the morphotropic phase boundary(MPB), which denotes an abrupt structural change with composition at constant temperature in a solid solution range. Since the coupling factor and dielectric constant of PZT become highest at compositions around the MPB, these compositions are widely exploited in commercial preparations of PZT ceramics and films.

Thin films of PZT and related compouds are playing an important role as basic elements in a variety of solid-state devices, the major interesting being in the non-volatile memories and actuators. In some applications, it is essential to prepare an oriented or epitaxial films with its polar axis perpendicular to the substrate surface.

Recently, epitaxial ferroelectric PZT films have been successfully grown by a number of deposition techniques such as chemical vapor deposition(2,3), rf sputtering(4,5), pulsed excimer laser deposition(6) and sol-gel method(7,8). Among them, the pulsed laser ablation deposition(PLAD) has recently gained great interest due to several benefits over the other deposition methods.

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Deposition rates of several microns per hour for PLAD can be easily achieved with reliable properties. The film composition can be also well controlled by adjusting the deposition parameters. In this paper, PLAD is used to deposit piezoelectric PZT thin films on Si wafer.

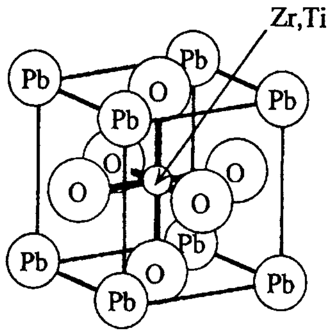

Fig. 1 The unit cell of $Pb(Zr,Ti)O_3$

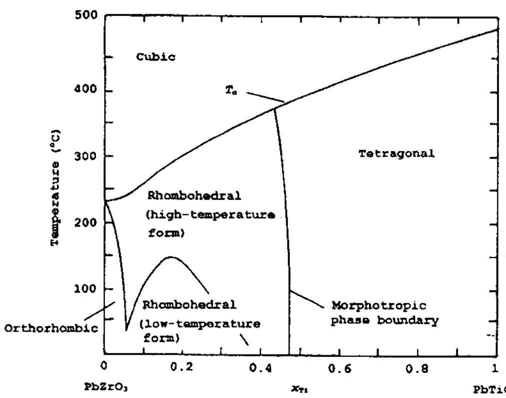

Fig. 2 Phase diagram of the $Pb(Zr,Ti)O_3$ system.

2. EXPERIMENTAL

2.1 Laser Apparatus

Fig. 3 shows the pulsed laser ablation system, which is composed of a laser source, and a deposition chamber with a 3 inch wafer substrate holder. A pulsed KrF excimer laser beam with wavelength 248nm, pulse repetition rate of 10Hz and energy of 600mmJ was focused through Quartz SUPRASIL II window. The pumping system is composed of rotary and turbo molecular pumps and the chamber could be evacuated to 10^{-7} Pa at room temperature. A fast atom beam source(Ion Tech Ltd., FAB110)is also available for substrate cleaning and atoms were supplied during deposition. Chamber pressure during FAB treatment was 1×10^{-3} Pa and applied voltage was 0.55 kV. The corresponding current was 10 mA. The distance between target and substrate is about 5 cm and both are rotated during deposition to improve the uniformity of thickness. The laser beam fluence was 1.2 J/cm^2 and the beam size was about $1\times3mm^2$.

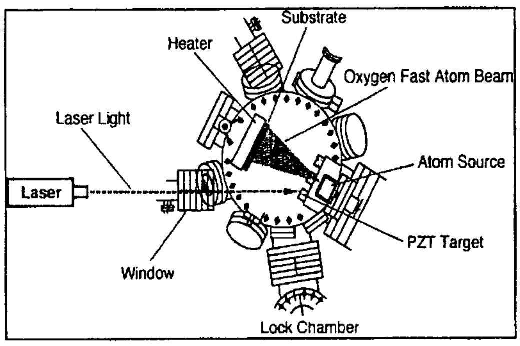

Fig. 3 Pulsed laser ablation deposition system

2.2 Specimen, process and measurement

A commercially available 3-inch size wafer was adopted for the substrate material. This is an n type semiconductor of (100) orientation. The target material was also commercially available PZT(Furuuchi Co. PZT F-13, reported value of relative permittivity 1800 and piezoelectric constant d_{31} 180, respectively) of morphotropic region $Pb(Zr_{0.52}Ti_{0.48})O_3$. The target was 20 mm in diameter and 5 mm in thickness. The specimens were oxidizes firstly untill the thickness of the oxide layer became 1.8 microns. Ti(50 nm)/Pt(150 nm) were deposted on the oxide to make the bottom electrode. The top electrode of Cr/Au(total thickness of 100nm) was formed by evaporation. The deposition rate was measured by a surface roughness meter(Ulvac Co., Dektak 3). Deposition was done under irradiation of oxygen FAB(oxygen gas pressure of 0.06Pa, 1kV, 30mA). After deposition, two-step annealing was done at atmospheric pressure with the temperature range of 600-750℃ and the holding time of 1-4 hours.

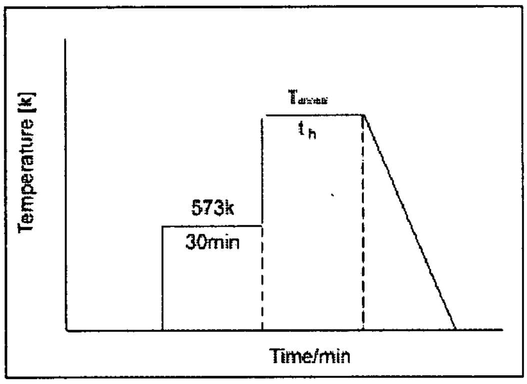

Fig. 4 Temperature profile of two step annealing

X-ray diffractmetry (Rigaku RINT-2500) was used for analysis of crystallographic structure of the deposited films. The P-E hysteresis loops of these films were measured using a standardized ferroelectric test system(Radiant Technologies RT-6000) which employs the principle of the Sawyer-Tower circuit. The dielectric constant and loss tangent values of these films were measured at 1 kHz using an LF impedance analyzer system (Hewlett-Packard HP4192A).

3. RESULTS AND DISCUSSION

The electrical properties have been investigated using a capacitor structure (Pt/PZT/Pt). Fig. 4 shows the hysteresis loop for the polarization of the PZT layer. The remanent polarization Pr was found to be 8.7 $\mu C/cm^2$ and the coercive field Ec was 33.6 kV/cm. The maximum polarization reached 19.3 $\mu C/cm^2$ at electrical field of 134 kV/cm. Measured value of the ε_r for this film is about 900. This value is rather satisfactory compared with other published data(9). The values of loss tangent for the samples were within the range of several %. The value of relative permittivity for the samples are much smaller than target. This is supposed to be the presence of the pyrochlore phase. The values of dielectric constant and remanent polarization in laser ablation deposited PZT thin films are lower than the respective values in bulk material, but still comparable to those of PZT thin films deposited by different methods. The electrical properties depend on film density, grain size and homogeneity of the thin film, etc. Mechanism to explain those differences have been proposed by Lappaninen et al recently(10).

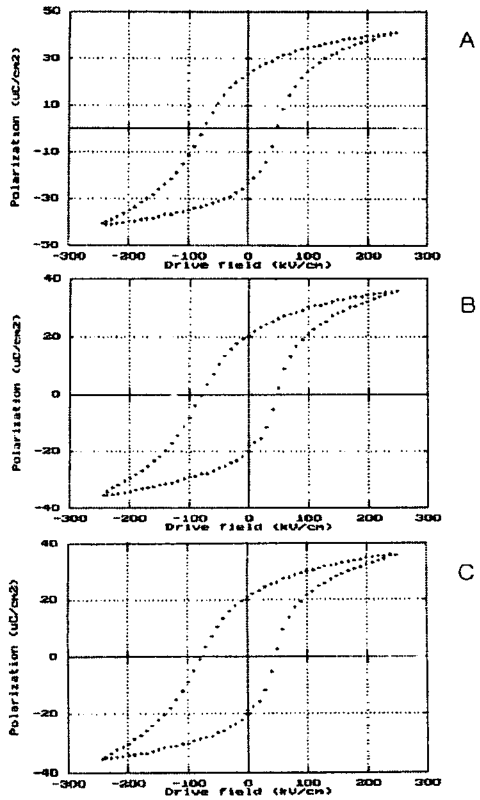

Fig. 5 The polarization vs. electric field hysteresis loop of the Pt/PZT/Pt capacitor structure. A:30min at 300℃ /1 hour at 600℃, B:30min at 300℃/1hour at 650℃, C:30min at 300℃/1 hour at 700℃

Fig. 5 shows XRD charts for different annealing conditions. PZT films deposited at room temperature have an amorphous structure. It was reported that, after annealing at 750℃, the perovskite structure was found with some amount of pyrochlore phase(11). The annealing temperature of 750℃ is rather higher, since such high temperature induces the peeling off of the deposited layer because oflarge thermal elongation. In order to obtain Perovskite phase at lower annealing temperature we attempt to change the annealing temperature profiles. After 1 hour of annealing at 650℃, highly (110) oriented Perovskite phase can be observed with little amount of Pyrochlore phase. Peeling of the deposited layer can be avoided at this annealing condition.

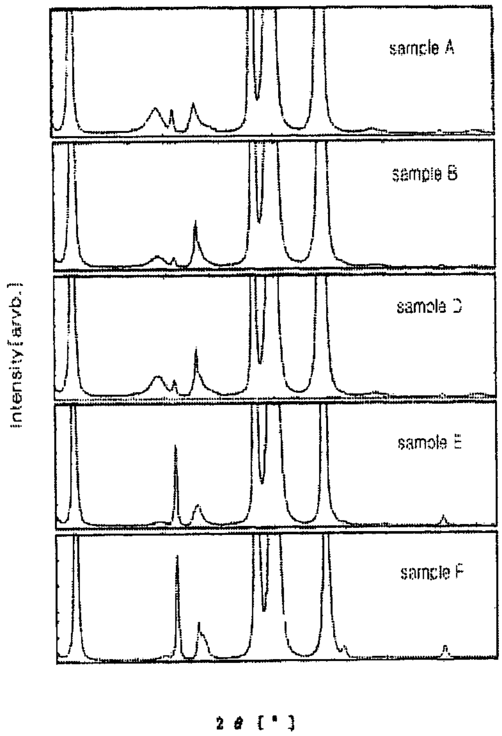

Fig. 6 XRD charts of PZT films annealed at various conditions. A:30min at 300℃/1 hour at 600℃, B:30min at 300℃/1hour at 650℃, D:30min at 300℃/1 hour at 750℃, E:30min at 300℃/2 hours at 600℃, F:30min at 300℃/4 hours at 600℃

4. CONCLUSION

PZT layers were prepared with pulsed laser ablation deposition method and the annealing effects were investigated. Although the overall characteristic values of PLAD PZT thin film are still small with respect to bulk material, we found that the perovskite structure would be appeared even after annealing at 923K as is the case of the 1023K. It can be concluded that the annealing temperature can be lowered up to 100K by two step abruptly changing temperature profile compared to that of conventional three step temperature profile.

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