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# Diode Laser Annealing of PZT Films Produced by Aerosol Deposition Method

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Lead zirconate titanate (PZT) films were produced on stainless steel substrate by the aerosol deposition method (ADM) using a PZT submicron-size particle beam. In the ADM, when the PZT submicron-size particles impact with the substrate, the particles form a film. To modify their primary ferroelectrics properties, the films were irradiated with a diode laser. When the scanning velocity of the laser spot on the films were decreased from 6 mm/s to 1 mm/s, laser intensity was increased from 110 W/cm$^2$ to 670 W/cm$^2$. Dielectric constant and the value of remanent polarization were improved by the laser irradiation. When the improvements of the properties were performed, the substrates were not damaged.
Key words: laser annealing, aerosol deposition method, ferroelectric properties, PZT film

## 1. INTRODUCTION

Lead zirconate titanate (PZT) films have numerous applications in very various devices such as micro actuator and ultrasound transducers [1-3]. There are some reports of the fabrication of PZT thick films by sol-gel[2], sputtering[3] and hydrothermal synthesis[4] methods. These conventional methods still have problems, such as the cracking in the film and easily peeling from the substrate, and need a long processing time for film fabrication.

The aerosol deposition method (ADM)[5], based on the gas deposition method[6], is expected to have a high deposition rate, high adhesion strength and high-density film formation. In the ADM, when submicron-size particles were accelerated by gas flow to velocities of several hundred m/s and collide with the substrate, a film was formed on the substrate. During formation of the film, neither the particles nor the substrate are heated. It is probable that a part of the particles' kinetic energy is converted during impact into thermal energy that promotes bonding between the particles and substrate. However, the actual bonding mechanism has not yet been elucidated.

PZT films have already been formed by ADM with high deposition rate, high density and good adhesion to the substrate [5]. However, post annealing is required to promote the grain growth and improve its ferroelectrics properties.

The dielectric constant of PZT ceramics can be varied by changing the grain size. When grain size is increased, the volume fraction of grain boundary and the domain density are decreased[7,8]. The coupling effect between the grain boundaries and the domain wall, which makes domain reorientation more difficult and severely constraints the domain wall motion, decreases as the grain size increases. Thus, the improvement of the dielectric properties due to grain growth is expected.

The film was annealed in an electric furnace. Then, the substrate was also heated. To avoid damaging the substrate, the film should be annealed without heating the substrate. The laser beam is focused to small area with focusing lens. Local area of the film is annealed by the laser beam focusing. When the laser energy is absorbed in the film, the substrate is not directly heated.

Diode lasers are widely used as a light source for laser printers, audio systems and optical communication systems because of their many advantages that include high conversion efficiency, small size, light weight, and a long lifetime. Recent advances have boosted both the output power and brightness of diode lasers through improvements in the laser diode itself and stacking technology.

In this paper, the effects of laser irradiation on ferroelectrics properties of the PZT films produced by ADM were investigated. We used a diode laser for this investigation.

## 2. EXPERIMENTAL CONDITIONS

System of the film fabrication by ADM was primarily composed of an aerosol chamber and a processing chamber connected with a tube, as shown in Fig. 1. The PZT particles' size was in the 0.1 to 1 μm range. An aerosol was produced by mixing the PZT particles with $N_2$ gas using a vibration system. The processing chamber was pumped down with a mechanical booster pump and a rotary pump to produce a pressure difference between the two chambers. $N_2$ gas flowed from the aerosol chamber to the processing chamber. The PZT particles were accelerated by the flow of $N_2$ gas and carried to the processing chamber through the tube and nozzle. The PZT particles ejected from the nozzle impacted with the substrate and were deposited on the substrate's surface. During the experiments the pressure difference between the two chambers was 1 atm. The nozzle employed in this experiment had a rectangular orifice of 10 x 0.3 mm in size. The substrates were stainless steel plates (SUS 304) with thickness of 2 mm, polished to a roughness (Ra) of around 0.04 μm. The distance between the nozzle and the stainless steel plate was 10 mm. The stainless steel plate's position was controlled with XYZ stages connected to a computer. An area of 7 x 8 mm on the surface of the stainless steel plate was scanned by the particle beam for 1 min at room temperature. Neither the stainless steel plate nor the PZT particles were heated during the coating process. The films with thickness of 3 μm were used for laser annealing tests, and used for evaluations of crystallinity and ferroelectric properties.

The wavelength of the diode laser used was 808 nm. The laser power was 17 W and not changed through the experiments. The laser was focused on the film at normal incidence. The laser beam spot on the film was oval shape, whose major and minor axes shown in Fig. 2 (a) were 1800 μm and 400 μm, respectively. The film was on the XY stages connected to a computer. The

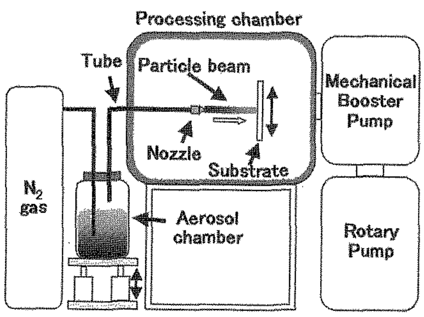


Fig. 1 Schematic configuration of film fabrication system utilizing ADM.

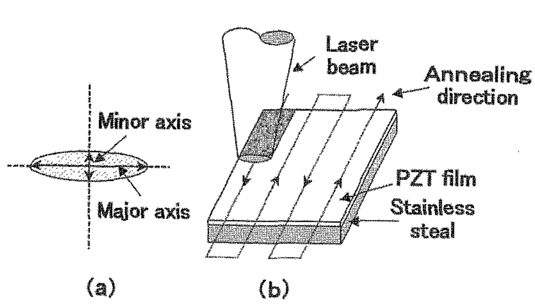


Fig. 2 (a) Shape of laser beam spot on the film. (b) Direction of laser annealing on the film.

laser beam spot was scanned to the direction on the minor axis as shown in Fig. 2 (b). As Fig. 2 (b) shows, four scanning were required to anneal the whole film. The scanning velocity was changed from 1 mm/s to 6 mm/s. Then, laser intensity was varied from 112 $W/cm^2$ to 674 $W/cm^2$ as the scanning velocity decreased. It took 32 s for annealing the film at the scanning velocity of 1 mm/s.

Thickness of the films was measured with a surface profiler. Crystallinity and microstructures of the as-deposited and laser annealed films were analyzed with X-ray diffraction (KRD, Rigaku Miniflex) and observed with scanning electron microscope (SEM, JEOL-6320), respectively. Au electrode was formed on the surface of the films for electric tests by using ion-sputtering apparatus (JEOL, JFC-1100E). P-E hysteresis loops were measured using ferroelectrics tester (Radiant technology, Precision LC) with high voltage interface (Radiant technology, HVA-2000). Dielectric constant and dielectric loss tangent were determined with LCR Hi-tester (HIOKI, 3532-50) by setting the oscillation level at 1V.

## 3. RESULTS AND DISCUSSION

Surface morphology of the PZT film produced by the ADM was shown in Fig. 3. The deposition rate was determined to be 3 μm/min from dependence of the film thickness on deposition time. The PZT film on substrate showed gray color as shown in Fig. 3. After polishing the deposited PZT films, metallic luster was obtained, indicating high density and small surface roughness. It was found that the films were dense from microstructure of cross section of the PZT film, which was similar to that of bulk PZT ceramics. After laser irradiation in the 112 to 674 $W/cm^2$ range, stainless steel plates were not damaged. The XRD patterns of the PZT powder used in this study and of the as-deposited PZT film and laser annealed PZT films are shown in Fig. 4. As laser intensity increased, the crystallinity of the film was improved. These results suggested that residual stress in the film was reduced or grain size was increased by laser annealing. Figure 5 (a) shows the variation of the

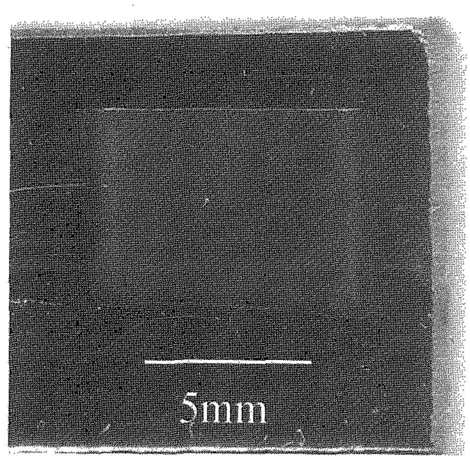


Fig. 3 Surface morphology of PZT film on substrate

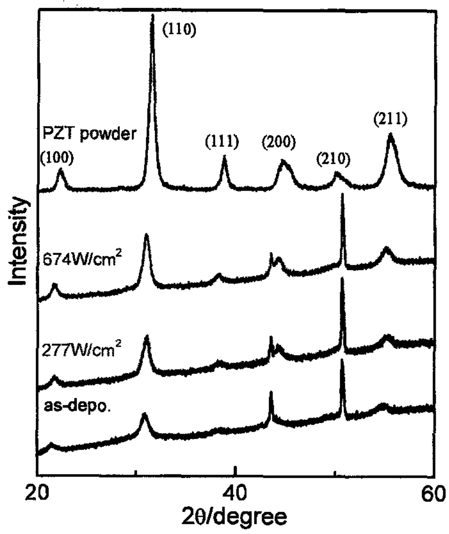


Fig. 4 X-ray diffraction pattern of PZT powder, the PZT film (as-depo.) formed on stainless steel plate, and laser annealed film at the laser intensities of 277 $W/cm^2$ and 674 $W/cm^2$.

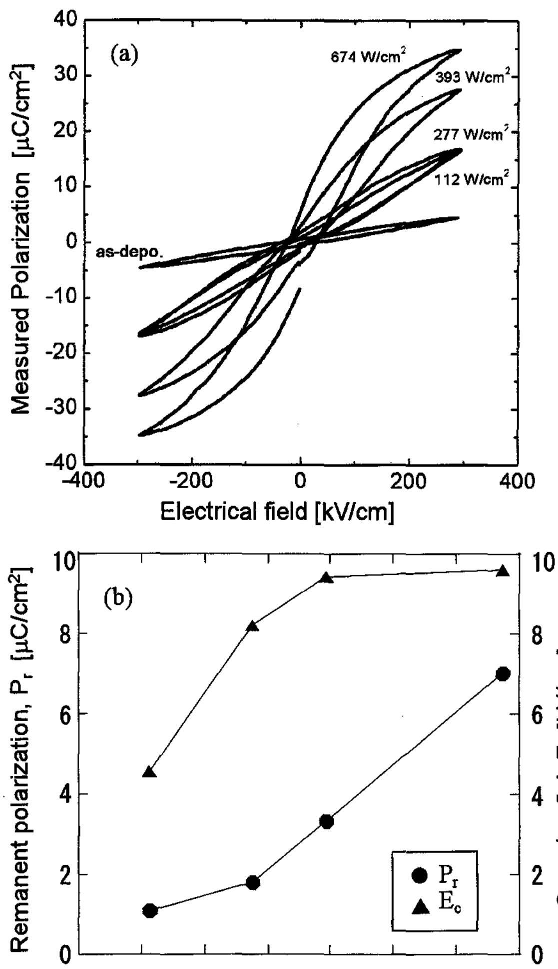


Fig. 5 (a) Hysteresis loop of the as-deposited and laser annealed PZT films, (b) remanent polarization ($P_r$) and coercive field ($E_c$) as a function of laser intensity.

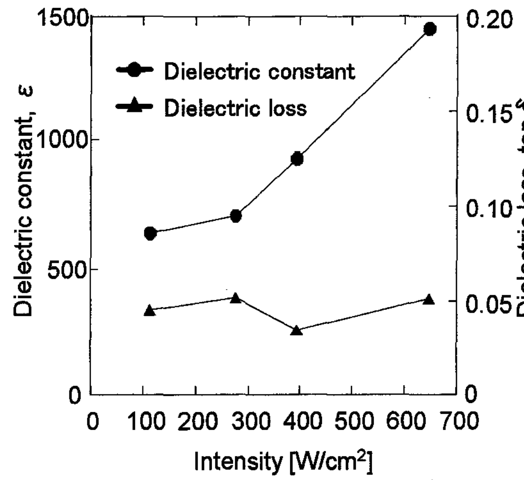


Fig. 6 Variation of the dielectric constant, $\varepsilon$, and dielectric loss, tan $\delta$, of the PZT films annealed by laser irradiation.

hysteresis loop of the as-deposited and laser annealed PZT films under electric field. The values of remanent polarization ($P_r$) and coercive field ($E_c$) as a function of the laser intensity were shown in Fig. 5 (b). As the laser intensity increased, the value of polarization at the electric field of 300 kV/cm, the $P_r$ and $E_c$ values were increased. At the laser intensity of 674 $W/cm^2$, the $P_r$ and $E_c$ values were 7.0 $\mu C/cm^2$ and 9.6 kV/cm, respectively. Variation of the dielectric constant and loss tangent of the PZT films by laser annealing were measured. These measurements were performed at the oscillation frequency of 1 kHz and the bias of 1 V. The value of the dielectric constant was calculated from capacitance of the films. Figure 6 shows variation of the dielectric constant, $\varepsilon$, and dielectric loss, tan $\delta$, of the PZT films annealed by laser irradiation. As Fig. 6 indicates, $\varepsilon$ was increased as laser intensity increased, and $\varepsilon$ was 1450 at 674 $W/cm^2$. Then, tan $\delta$ was not increased.

When the PZT film was annealed using electric furnace at 873 K for 1.8 ks, the $P_r$, $E_c$ and dielectric constant were increased [9]. The $P_r$ and $E_c$ values were 6.0 $\mu C/cm^2$ and 10.8 kV/cm, respectively. The dielectric constant value was in the 700 to 800 range. These results indicate that the annealing using electric furnace could improve the $P_r$, $E_c$ and the dielectric constant. However, the substrates were damaged by oxidization due to heating in electric furnace. Annealing time for electric furnace, 1.8 ks, was much longer than that for laser irradiation, 32 s.

When the laser irradiated the PZT film surface at 674 $W/cm^2$, temperature at the backside of the stainless steel plate was about 400 K, much lower than 873 K for heating using electric furnace. At the scanning velocity of 0.8 mm/s, over 674 $W/cm^2$, PZT film was ablated by the laser although stainless plate surface was not ablated then. These results also suggested that laser energy was absorbed in the PZT film.

## 4. CONCLUSION

The ferroelectrics properties of the PZT film produced by ADM were successfully improved by diode laser irradiation. The $P_r$, $E_c$ and the dielectric constant were increased as the laser intensity increased. Annealing velocity for the improvement was much faster than that by heating using electric furnace. The substrates were not damaged through the laser annealing process.

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