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CO_2 Laser Annealing Effect of Electrical Properties and Microstructures on $Pb(Zr,Ti)O_3$ Thick Films Prepared by Aerosol Deposition

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Lead zirconate titanate (PZT) thick films have been produced by aerosol deposition method (ADM) for a part of manufacture of micro-pumps, ultrasonic mixers in new micro electromechanical systems (MEMS) and micro-total analysis systems (μ-TAS), micro-actuator, ink-jet printer heads, flapper actuators for high-density hard-disk drive and others. As-deposited PZT films by ADM do not have enough ferroelectric and/or piezoelectric properties as above applications. For increasing the film properties, rapid thermal annealing (RTA) process like a laser radiation are expected. The laser can be focused and/or scanned suitably only on necessary part of system-on-a-chip (SoC) with some mirrors and lenses, and be introduced from the outside of deposition chamber through the glass window, so the deposition conditions are not almost affected by the laser radiation. Especially CO_2 laser (λ = 10.6 μm), which has been reported to have a good absorption for the PZT films, are more excellent oscillation efficiency and running cost than YAG laser which is the same infrared laser. In this study, we discussed the effect of electrical properties and microstructure of PZT films prepared by ADM on the CO_2 laser annealing.

Key words: PZT, thick film, stainless steel substrate, aerosol deposition, CO_2 laser annealing

1. Introduction

$Pb(Zr,Ti)O_3$ (PZT) films deposited on substrate by aerosol deposition method (ADM) using an impact consolidation of primary powder particles, which have almost single-crystal structure and their crystallite size is estimated to be from 100 nm to 500 nm, are usually annealed by electric furnace for grain growth and defect recovery because as-deposited films are consisted of microstructure of randomly oriented small crystallites in sizes of 100 nm to 300 nm, which are close to those observed in the primary powder. In the case of $PZT/Pt/Al_2O_3$ structure, almost the same hysteresis loops as the bulk PZT ceramics can be available by post-annealing with electric furnace at 850 °C for 1 hr [1]. But using low-melting substrates such as stainless steel and/or plastic, PZT/substrate structure can not be annealed at such a high temperature because the heat damages are given to the other parts of the film.

Infrared (IR) laser shows an absorption to not the metal but the almost ceramics. Moreover, the laser can be focused and/or scanned suitably only on necessary part of devices with some mirrors and lenses, and be introduced from outside of the deposition chamber through the glass window, so the deposition conditions are not almost affected by the laser radiation. Especially CO_2 laser (λ = 10.6 μm), which has been reported [2] to have a good absorption for the PZT and PLZT films, are more excellent oscillation efficiency and running cost than YAG laser which is the same IR laser. So the CO_2 laser can be practically irradiated to only the part of the film.

In this study, we introduce the first report which researches the effect of the CO_2 laser radiation on the film deposited on the stainless steel substrate by ADM.

2. Experimental Procedure

Figure 1 shows the schematic configuration of the ADM with the CO_2 laser radiation. The PZT films were deposited on SUS304 stainless steel substrates with the thickness of 100 μm by the ADM. The substrate surface was not polished particularly and was fixed to a substrate holder connected with *X-Y-Z* stage in the deposition chamber, and was scanned at the speed of 1.25 mm/s and 0.3125 mm/s in the direction of one axis. Commercially available raw-material powder (PZT-LQ: niobium-modified PZT, Sakai Chemical Ind.) was used. The PZT powder had a perovskite structure and a composition of $Pb(Zr_{0.52},Ti_{0.48})O_3$, which was close to that of the morphotropic phase boundary. As the carrier gas, Helium (He) was used. The gas consumption was 2.5 ℓ/min. The deposition pressure was almost 40 Pa. Aerosol-jet, which was consisted of PZT powders mixed with He gases, was ejected from nozzle with orifice of 10 x 0.4 mm^2 on the surface of the substrate. The distance between the nozzle and the substrate was 10 mm and 25 mm.

After or during the film deposition, the films were annealed within and/or without the deposition chamber. One of the films was post-annealed by an electric furnace at 600 °C for 1 hr. in an air. The other films were irradiated by CO_2 laser (SYNRAD, 48-1) with a wavelength of 10.6 μm and with a beam diameter of 4 mm. After the film deposition, the laser was post-annealed the film surface with or without a

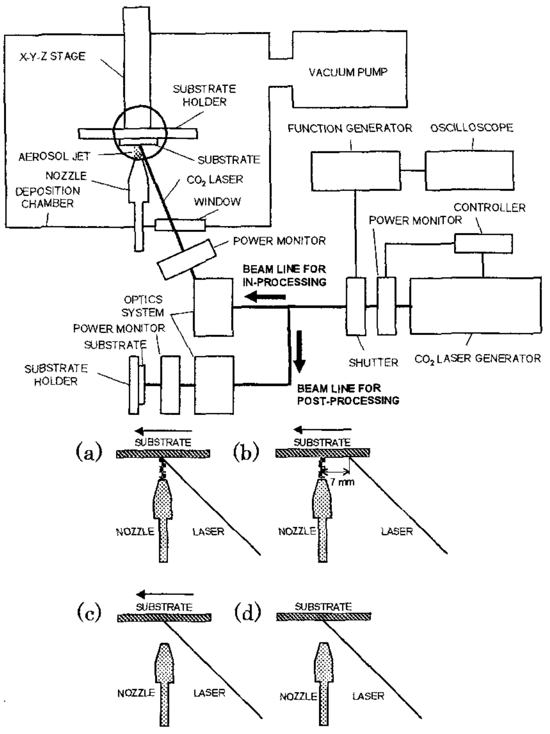

Fig.1 Experimental set up of aerosol deposition method with laser radiation within and without the chamber. The laser is irradiated to the film during the deposition [(a) and (b)] and after the deposition [(c) and (d)].

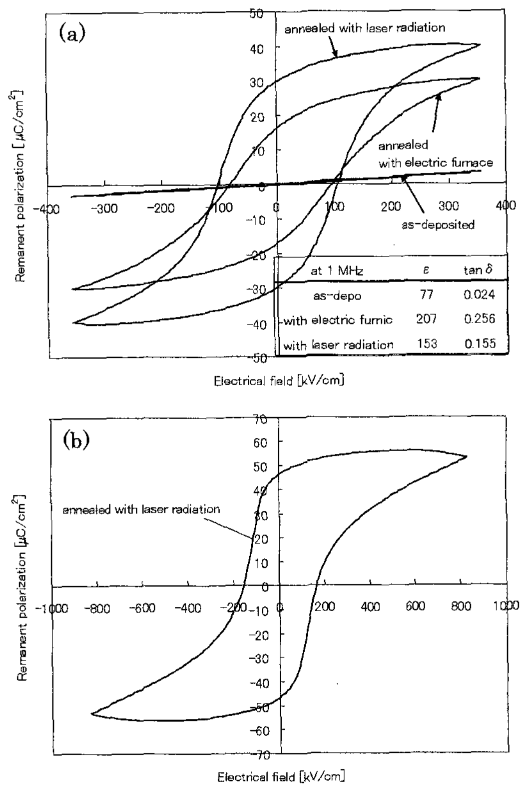

Fig.2 Hysteresis loops of PZT films deposited on SUS304 stainless steel substrates with and without post-annealing. (a) Comparison of the hysteresis loops between the post-annealing processes and (b) Hysteresis loop of the film post-annealed by the laser radiation applied at maximum electrical field.

scanning of the substrate in the deposition chamber. The laser was irradiated to the film surface of the bombardment of an aerosol-jet or 7 mm away during the film deposition.

For electrical measurements, Gold (Au) (1 mm^2) and/or silver (Ag) paste (~ 4 mm^2) upper electrode was fabricated on the top of the PZT films. The dielectric permittivity was measured by an impedance analyzer (HP4194) operated at 0.5 V. The Hysteresis loops were determined with the virtual ground method (TF-ANALYZER 2000, AixACCT).

3. Results and discussion

After the film deposition at the scanning speed of 1.25 mm/s and the distance between the nozzle and the substrate of 10 mm, the films were post-annealed by the electric furnace or the laser radiation at an energy density of 52 J/mm^2. Using electric furnace, substrate surface was changed colors from metallic luster to oxidization. On the other hand, only the film surface and opposite side were annealed and changed colors by laser radiation. Figure 2 shows the variation of the ferroelectric hysteresis loops of PZT films deposited on SUS304 stainless steel substrates with and without post-annealing in an air. The film thickness was 3.5 μm. The applied maximum electrical field was 350 kV/cm. As-deposited film does not show the ferroelectric properties clearly because of the composition of the nano-structure and the inclusion of any defects. On the other hand, the remanent polarization and the coercive field were dramatically increased with the electric furnace at 600 °C for 1 hr. reached 16 μC/cm^2 and 100 kV/cm, respectively. Using the laser radiation, the remanent polarization of the post-annealed film was reached 46 μC/cm^2. Meanwhile, the dielectric dissipation factor of the films was not so good. It seems that the heat influence causes the formation of the diffusion layer and/or the degradation of the adhesiveness between the film and the substrate. From these results, it is clear that the CO_2 laser post-annealing is better than conventional method from the view point of the improvement of the remanent polarization. It is difficult to measure a temperature of PZT film irradiated by the CO_2 laser because the emissivity of the PZT film deposited by the ADM and irradiated by the laser is unknown. Thus, the temperatures of the back side of the substrate with and without various thicknesses of PZT films during the laser radiation was determined with K-type thermocouple. The temperature of the back side of the substrate without the PZT film was heated up to only 120 °C. On the other hand, those of the substrates with the film was heated over 200 °C, especially 4~5 μm-thick and 45 μm-thick PZT films were heated up to almost 300 °C and 600 °C, respectively. It is found that the substrate temperature is increased by increasing the volume of the PZT film with absorption of laser power.

While, from SEM observation of the film, a little grain growth and a necking between the grains were affirmed. It seems that the conditions of the laser

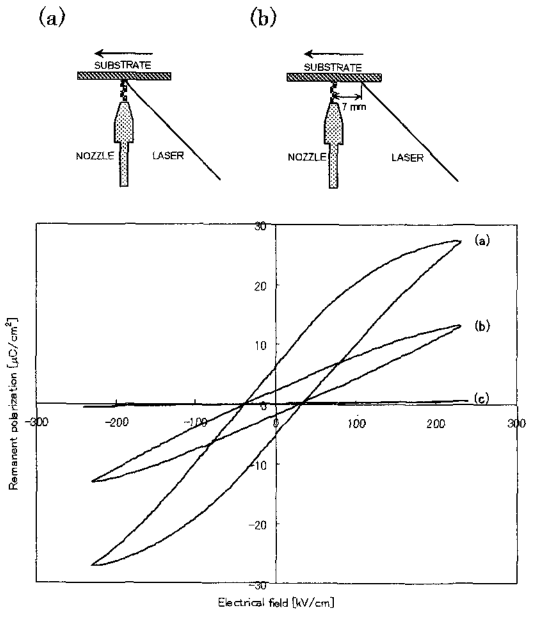

Fig.3 Hysteresis loops of PZT films deposited on SUS304 stainless steel substrates irradiated the CO_2 laser during the film deposition. Post-annealed films [(a) and (b)] and As-deposited film (c)

radiation in this research are not enough for promotion of the grain growth in equal to that of the bulk ceramics.

Dielectric permittivity of the film annealed by the laser radiation is lower than that by the electric furnace in spite of the superior value of the remanent polarization. This result makes us suggest that the laser radiation under the PZT/SUS304 structure induced not only the leak current because the film-peeling has been partially generated for a heat-shock because of a rapid hating and a quenching but also the different microstructure compared with the electric furnace heating.

In the deposition chamber, the laser was irradiated to the film during or after the film deposition for almost 5 min. The laser power density was 324.4 J/mm^2. The substrate was scanned within the range of 7 mm at the speed of 0.3125 mm/s and the distance between the nozzle and the substrate was 25 mm. After the film deposition, all of the films post-annealed by the laser radiation were peeled off from the substrate. On the other hand, the films irradiated by the laser radiation during the film deposition were deposited on the substrate without the peeling. These results mean that the limit of the film thickness to which the laser can be irradiated exists due to the thermal expansion coefficient between the film and the substrate. Figure 3 shows the variation of the ferroelectric hysteresis loops of the films annealed by the laser radiation during the film deposition compared with that of the as-deposited film. The ferroelectric properties of the film by which the laser irradiated to the surface of the film at the point of the collision of the aerosol-jet (type-A) is better than those separated 7 mm away from the jet (type-B). It seems that the synergy effect of an annealing of the film and the particle growth before and/or after the film deposition are improved the electrical properties of films because the wavelength of the CO_2 laser is larger than the size of the aerosol-particles.

Figure 4 and 5 show the variation of the ferroelectric hysteresis loops and the dielectric properties of the films annealed by the laser radiation (type-A) with the different power density during the film deposition for almost 5 min. The substrate was scanned within the range of 10 mm at the speed of 0.3125 mm/s and the distance between the nozzle and the substrate was 25

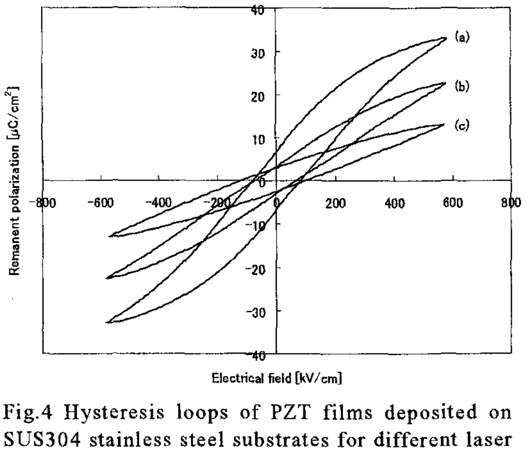

Fig.4 Hysteresis loops of PZT films deposited on SUS304 stainless steel substrates for different laser radiation of energy density during the film deposition. (a) 324.4 J/mm^2, (b) 302.0 J/mm^2 and (c) 227.1 J/mm^2

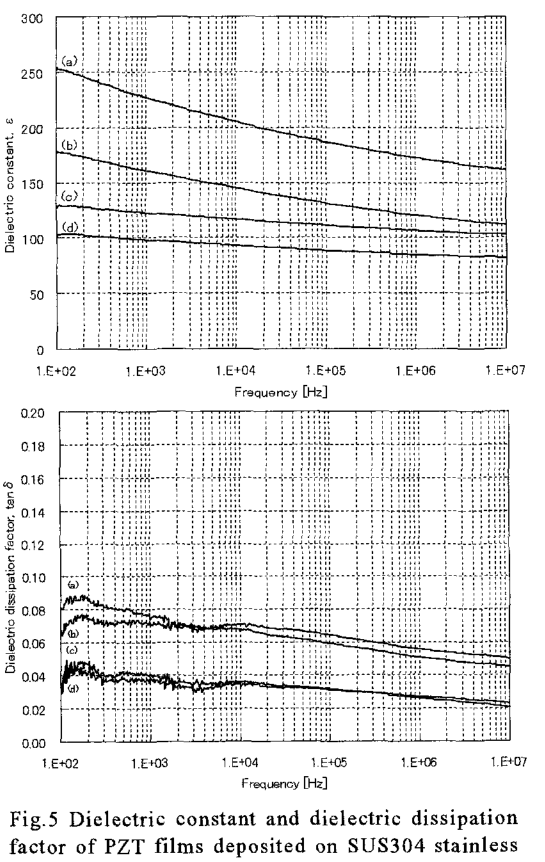

Fig.5 Dielectric constant and dielectric dissipation factor of PZT films deposited on SUS304 stainless steel substrates for different laser radiation of energy density during the film deposition. (a) 324.4 J/mm^2, (b) 302.0 J/mm^2, (c) 227.1 J/mm^2 and (d) as-deposited film.

mm. The film thickness was 5-7 μm. The frequency dependence of the dielectric properties of the films is not so large as same as-deposited film. Especially, the dielectric dissipation factor of the films at 1 MHz is better than that of the post-annealed film and increased with increasing the laser power density. It makes us suggest that the adhesiveness were decrease because of the shear stress between the film and the substrate due to the different thermal expansion coefficient. The ferroelectric properties and the dielectric constant of the films are increased with increasing the laser power density, but are inferior to those of the post-annealed films in spite of much higher laser power density. During the film deposition, the film and the substrate are cooled down by a carrier gas and the aerosol jet with an adiabatic expansion. Thus, it is considered that the thermal conductivity of an atmosphere during the laser radiation is decrease due to a lower gas pressure compared with an ambient pressure, so much higher laser power density is required to achieve a same effect of the post-annealing with the laser radiation.

4. Summary

1. The CO_2 laser annealing is the powerful tool for improvement of the electrical properties of the PZT films.
2. To avoid the peeling of the film from the substrate, there is the proper film thickness for the CO_2 laser radiation.
3. To anneal the PZT film by CO_2 laser radiation during the film deposition, it is necessary for consideration of a thermal balance of the film and substrate under the laser radiation.

Acknowledgements

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