AIP | Applied Physics Letters

Laser-assisted low temperature processing of Pb(Zr,Ti)O 3 thin film

Yongfei Zhu, Jinsong Zhu, Yoon J. Song, and S. B. Desu

Citation: Applied Physics Letters **73**, 1958 (1998); doi: 10.1063/1.122334
View online: http://dx.doi.org/10.1063/1.122334
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/73/14?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS VOLUME 73, NUMBER 14 5 OCTOBER 1998

Laser-assisted low temperature processing of Pb(Zr, Ti)O_3 thin film

Yongfei Zhu,[a] Jinsong Zhu, Yoon J. Song, and S. B. Desu[b]
Department of Materials Science and Engineering, Virginia Tech, Virginia 24061

(Received 5 December 1997; accepted for publication 1 August 1998)

A method for lowering the processing temperature of $PbZr_{1-x}Ti_xO_3$ (PZT) films was developed utilizing a laser-assisted two-step process. In the first step, perovskite phase was initiated in the PZT films to a furnace anneal at low temperatures in the range of 470–550 °C, depending on the Zr/Ti ratio. Later, the films were laser annealed (using KrF excimer laser) at room temperature to grow the perovskite phase, and to improve microstructure and ferroelectric properties. It was found that this two-step process was very effective in producing excellent quality ferroelectric PZT films at low temperatures. It should be noted that although laser annealing of amorphous and/or pyrochlore films directly (one-step process) produced perovskite phase, the ferroelectric properties of these films, irrespective of the composition, were rather unattractive. Some possible reasons for the ineffectiveness of the one-step process were discussed. © *1998 American Institute of Physics.* [S0003-6951(98)02640-0]

Perovskite thin films such as $PbZr_{1-x}Ti_xO_3$ (PZT) have a wide range applications due to their ferroelectric, pyroelectric, electro-optic, and piezoelectric properties.[1–3] Their multifacted properties along with the possibility of integrating these films with standard complementary metal-oxide-semiconductor (CMOS) devices have ignited considerable interest for producing integrated devices such as nonvolatile memories and high efficiency infrared sensors. However, the production of CMOS devices such as integrated pyroelectric infrared detectors places significant constraints on the ferroelectric film fabrication process. Currently, temperatures of about 650 °C are required to obtain good quality PZT films whereas, processing temperatures in the range of 450–550 °C will significantly increase the yields as well as improve the performance and reliability of these integrated devices. Although the process temperatures are high, use of rapid thermal processing (RTA) techniques have been proposed for reducing the total thermal budget for depositing ferroelectric films. In contrast, here we will report a novel laser-assisted technique for lowering the process temperature to less than 550 °C.

Although, laser-assisted crystallization of amorphous Si is well known,[4,5] its application to ferroelectric films is very recent.[6–8] These recent reports indicated that amorphous PZT films can be crystallized at room temperatures using excimer lasers. However, no ferroelectric properties have been reported for these laser crystallized films. Since laser annealing is very attractive in terms of low substrate temperature, selective annealing area, and short duration time, we have investigated film properties as a function of laser annealing conditions for developing a low temperature ferroelectric film fabrication process.

In this study, PZT films were prepared by modified sol-gel technique.[9,10] Precursors were Zr *n* propoxide, Ti isopropoxide and Pb acetate, and the solvents were acetic acid and propanol. PZT films with thickness of 170 nm were deposited on Pt/Ti/SiO_2/Si substrates. The laser annealing was performed with the use of a KrF excimer laser (wavelength of 248 nm). The pulse width and repetition frequency of the laser beam were 30 ns and 20 Hz, respectively. During the laser annealing, the sample was under ambient conditions.

For electrical measurements, Pt top electrodes with area of 3.8×10^{-4} cm^2 were deposited on the films by sputtering. The films were characterized for thickness by variable angle spectroscopic ellipsometry, for phase formation by x-ray diffraction (XRD), for microstructure by atomic force microscopy (AFM), and for ferroelectric properties by standardized RT66A tester and operation in a Virtual-Ground mode.

In the first part of our experiments, amorphous and/or pyrochlore PZT thin films were directly laser annealed (one-step process) to convert them into ferroelectric perovskite phase. Laser energy density were varied from 50 to 200 mJ/cm^2 per pulse, and the number of pulses were varied from 10 to 1000. The laser annealed films showed weak perovskite peaks. Figure 1 shows a XRD pattern of the laser annealed film at an energy density of 80 mJ/cm^2 and 100 pulses, the pattern is similar to the results of those shown in

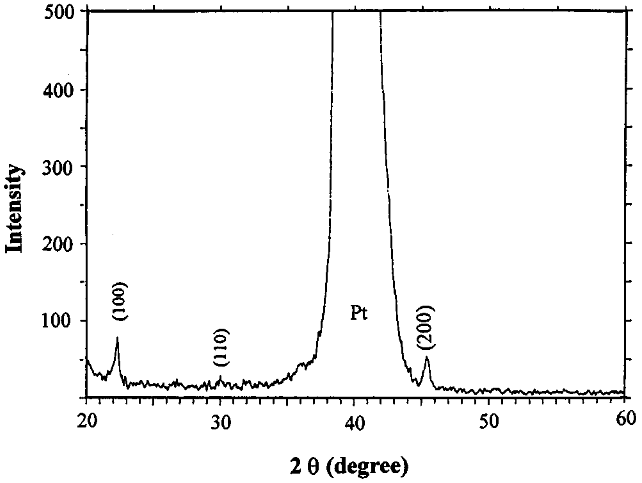

FIG. 1. XRD pattern of PZT(53/47) film after directly laser annealing.

---

[a] Corresponding author.
[b] Electronic mail: sdesu@vt.edu

Refs. 6 and 7. No hysteresis loops were obtained from these films. It was found that the film surface became rougher when either higher energy densities or a larger number of pulses were used. For example, five pulses with an energy density at 150 mJ/cm^2 made the PZT film very rough. This indicates that PZT is being ablated during this process.

We also found that the absorption edge of PZT is about 350 nm and there is a strong absorption at the KrF laser wavelength of 248 nm. This indicates that most irradiation energy is absorbed on the top surface of the film, which facilitates top surface ablation, and limits the crystallization depth of the film. We feel that the weak perovskite peaks in the XRD pattern of the directly laser annealed films were due to the contribution of the top layer of PZT film. It is known that the PZT perovskite formation from amorphous and/or pyrochlore phase is nucleation dominated. The activation energy of nucleation is about four times the activation energy of growth of the perovskite.[11] In other words, the grain growth of the perovskite phase is much easier than direct transformation of perovskite from amorphous and/or pyrochlore phase.

Therefore, we can conclude that obtaining ferroelectric properties by directly laser annealing of amorphous and/or pyrochlore films is difficult. This may be attributable to: (1) very low energy threshold of ablation of PZT,[12] (2) very thin absorption depth at 248 nm wavelength, and (3) high energy required for the nucleation of the perovskite phase.[11]

Since the nucleation of the perovskite phase may be difficult by laser annealing below the ablation energy threshold, we proceeded to nucleate perovskite phase by thermal processing and grow the perovskite grains by laser annealing (two-step process). The as-coated sol-gel PZT films with Zr/Ti ratios of 53/47, 40/60, 30/70, and 20/80 were furnace annealed at temperatures of 550, 525, 500, and 475 °C, respectively. The furnace annealed films showed similar XRD pattern with strongly perovskite (111) preferred orientation without pyrochlore peaks. Figure 2(a) shows a typical XRD pattern of PZT (30/70) after furnace annealing at 500 °C for 1 h in oxygen atmosphere. Later, the furnace annealed films were subjected to laser annealing with 70 mJ/cm^2 for 100 pulses, the film shows again the (111) preferred orientation with higher intensity in its XRD pattern [shown in Fig. 2(b)]. This indicates that the crystallization of the film is enhanced by the laser annealing.

In addition, laser annealing also significantly increased the grain size of these films. Figure 3 shows the AFM surface morphology of PZT (30/70) films before Fig. 3(a) and after Fig. 3(b) laser annealing in the two-step process.

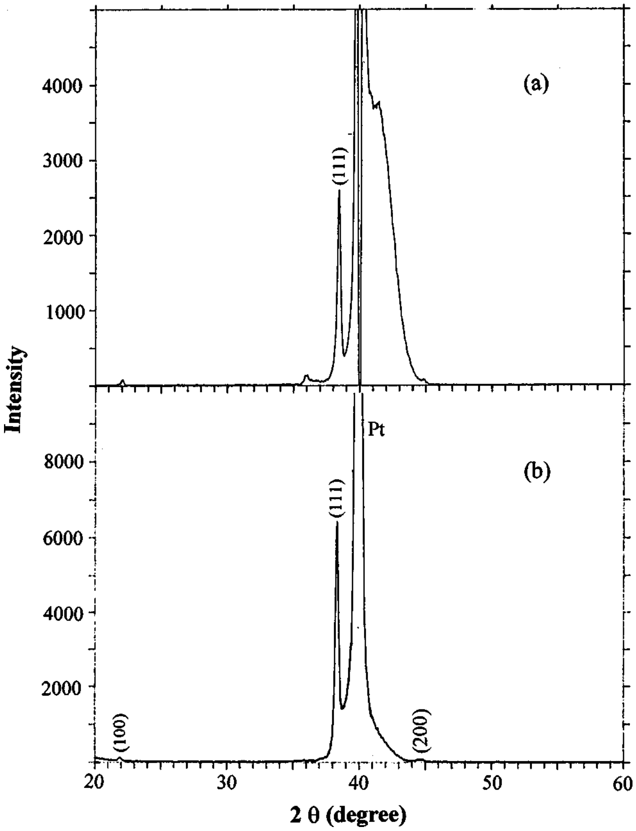

FIG. 2. XRD pattern of PZT(30/70) film before (a) and after (b) laser annealing in the two-step process.

Figure 4 shows the hysteresis loops of films after furnace annealing and laser annealing, respectively. After the furnace annealing, the films show hysteresis loops (shown in solid circles) with low remanent polarization (P_r) and high coercive voltage (V_c), and the loops do not saturate well especially for higher Ti content PZT films. It can be seen in Fig. 4 that the higher the Ti content of the film, the higher the remanent polarization and the higher the coercive voltage. After laser annealing, the films show highly saturated hysteresis loops (shown in empty triangles in Fig. 4). The P_rs increase from 16.8 to 42.6 μC/cm^2 for PZT(20/80), 22.6 to 36.7 μC/cm^2 for PZT(30/70), 12.4 to 34.1 μC/cm^2 for PZT(40/60), and 10.34 to 30.3 μC/cm^2 for PZT(53/47). The V_cs decrease from 4.8 to 3.3 V for PZT(20/80), 3.4 to 2.5 V for PZT(30/70), 2.6 to 2.4 V for PZT(40/60), and 2.2 to 2.1 V for PZT(53/47). It is noted that the coercive voltages of all the samples with thickness of about 170 nm are higher than those of films annealed by conventional furnace at higher

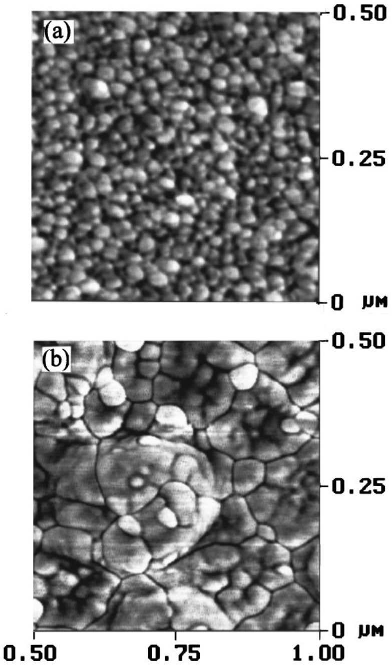

FIG. 3. AFM surface morphology of PZT(30/70) film before (a) and after (b) laser annealing in the two-step process.

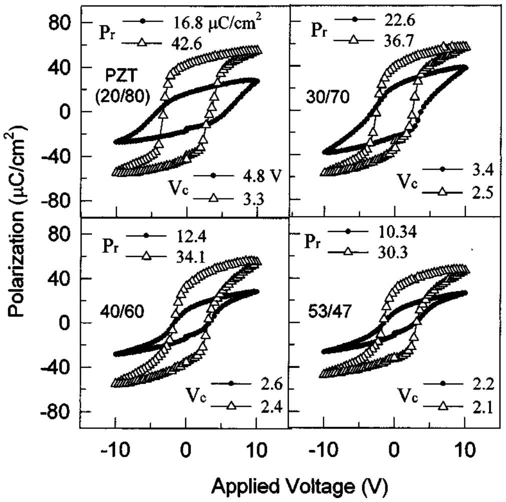

FIG. 4. Hysteresis loops of PZT films before (solid circles) and after laser annealing (empty triangles) in the two-step process with various Zr/Ti ratios. The furnace annealing temperatures were 475 °C for PZT(20/80), 500 °C for 30/70, 525 °C for 40/60, and 550 °C for 53/47.

temperature. We believe that the problem is caused by the small grain size and/or unannealed lower layer of the films because of thin crystallization depth.

In summary, a novel method was developed for lowering the processing temperature of ferroelectric $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ (PZT) thin films using a laser-assisted two-step process. In the first step, the PZT films were crystallized into perovskite phase by annealing the films in a tube furnace at low temperatures ranging from 470 to 550 °C depending on the Zr/Ti ratio. The second step was to laser anneal the heat-treated PZT films using KrF excimer laser at room temperature for growing the perovskite phase and enhancing microstructure and ferroelectric properties. The PZT films prepared by the two-step process were found to exhibit excellent ferroelectric properties at low temperatures. The direct laser annealing of amorphous and/or pyrochlore films (one-step process) was carried out to produce perovskite phase, but the ferroelectric properties of these films were rather unattractive, which might be attributed to easy ablation, thin absorption depth, and high perovskite formation energy of the PZT film.

This work was supported by the U.S. Defense Advanced Research Projects Agency (DARPA).

[1] J. F. Scott and C. A. Paz de Araujo, Science **246**, 1400 (1989).
[2] M. Okuyama and Y. Hamakawa, Ferroelectrics **63**, 243 (1985).
[3] A. Mansingh, Ferroelectrics **102**, 69 (1990).
[4] A. Gat, L. Gerzberg, J. F. Gibbons, T. J. Magee, J. Peng, and J. D. Hong, Appl. Phys. Lett. **33**, 775 (1978).
[5] H. Watanabe, H. Miki, S. Sugai, K. Kawasaki, and T. Kioka, Jpn. J. Appl. Phys., Part 1 **33**, 4491 (1994).
[6] X. M. Lu, J. S. Zhu, X. F. Huang, C. Y. Lin, and Y. N. Wang, Appl. Phys. Lett. **65**, 2015 (1994).
[7] X. M. Lu, J. S. Zhu, W. S. Hu, Z. G. Liu, and Y. N. Wang, Appl. Phys. Lett. **66**, 2481 (1995).
[8] S. B. Xiong, Z. M. Ye, J. M. Liu, A. D. Li, C. Y. Lin, X. Y. Chen, X. L. Guo, and Z. G. Liu, Appl. Phys. Lett. **109/110**, 124 (1997).
[9] G. Yi, Z. Wu, and M. Sayer, J. Appl. Phys. **64**, 2717 (1988).
[10] Yoon J. Song, Yongfei Zhu, and S. B. Desu, Appl. Phys. Lett. **72**, 2683 (1998).
[11] C. K. Kwok and S. B. Desu, J. Mater. Res. **9**, 1728 (1994).
[12] D. J. Linchtenwalner, O. Auciello, R. Dat, and A. I. Kingon, J. Appl. Phys. **74**, 7497 (1993).