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Control of Nucleation and Grain Growth Processes in Lead Zirconate Titanate Thin Films

Jang-Sik Lee*

School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Korea

We found that single grains as large as 40 μm in length of lead zirconate titanate (PZT) thin film could be fabricated by lateral crystallization from the seeds. The seeds were prepared on a Pt substrate in the form of crystallized PZT dots. The electrical characteristics of PZT thin films obtained by selectively nucleated lateral crystallization (SNLC) were found to be superior to those of polycrystalline PZT thin films. In this paper, we review the mechanism for SNLC. From investigation into the nucleation and grain-growth processes in PZT thin films, we devised a novel annealing method that is suitable for SNLC of PZT thin films. It was found that scanning-rapid thermal annealing is a very effective method for SNLC in terms of reducing the process time and preventing undesirable nucleation in regions outside of pre-determined nucleation sites.

Keywords: lead zirconate titanate (PZT), nucleation, grain growth, thermal annealing

1. INTRODUCTION

Variation in the microstructure of crystalline materials has a significant impact on the electrical, mechanical, magnetic or optical properties of devices and components to which they are applied[1]. A major concern regarding the microstructure is the geometric arrangement of the grains, because randomly distributed grains or grain-boundary configurations result in non-uniform characteristics of the devices. The best solution to overcome spatial non-uniformity problems originating from grain-boundaries is to fabricate single-crystal thin-film materials; however, the fabrication process for single crystalline films is too complicated to be adopted in conventional semiconductor processes[2].

For the last few decades, extensive research on metal-oxide thin films with respect to memory device applications has been conducted. In particular, many studies have been carried out on capacitor materials, such as Ta_2O_5, Al_2O_3, $(Ba,Sr)TiO_3$, $Pb(Zr,Ti)O_3$, $SrBi_2Ta_2O_9$, etc. in efforts to realize high performance storage capacitors of dynamic random access memory (DRAM) and ferroelectric random access memory (FRAM). In this field, materials with crystalline structure are preferred over amorphous materials, because the crystalline materials can increase the charge storage density and carrier transport of DRAM and FRAM. However, as the size of the storage capacitors becomes smaller in compliance with nano-technology, the non-uniform characteristics of crystalline material based devices present new challenges.

The advent of nano-technology is expected to reduce the device size to the order of or smaller than the PZT grains. This, in turn, increases the importance of the geometry of the grains, including the number of grains and grain boundaries per unit device area. Devices with smaller features show a relatively significant change in the number of grains within an individual cell compared to those with larger features. This indicates that smaller devices have greater likelihood of non-uniform function and decreased reliability. Therefore, it is of considerable importance to determine a means of finely controlling the effects of grain boundaries on the electrical properties in small devices.

We previously reported on the selectively nucleated lateral crystallization (SNLC) of $Pb(Zr,Ti)O_3$ (PZT) thin films and their electrical characteristics[3-8]. Using the SNLC method, we could control the nucleation site, and thereby the grain-location in PZT thin films. SNLC is based on selective nucleation and grain growth between the template layer and the perovskite seed. SNLC annealing is carried out in a conventional diffusion furnace. However, the selective growth of large grains in a conventional furnace is practically limited in the sense that the annealing temperature should be low enough to prevent undesirable nucleation at the unseeded region. However, due to the low annealing temperature, the growth rate of large grains is small. Even when the annealing temperature is lower than the normal growth temperature of the PZT grains, there remains undesirable nucleation at sites where pre-treated seeds are not present. In the present study, a new annealing method, scanning-rapid thermal annealing

*Corresponding author: jangsik@kookmin.ac.kr

(RTA), is used in order to prevent undesirable nucleation by reducing the process time. We also review the mechanism for SNLC of PZT films and discuss the effect of scan-lamp power and scan speed on the crystallization behavior of the films.

2. EXPERIMENTS

$Pb(Zr_{0.65}Ti_{0.35})O_3$ thin films were formed on $Pt/SiO_2/Si$ substrates by rf magnetron sputtering at 350°C using multi-metal targets of Pb, Zr, and Ti. The base pressure before sputtering was below 1×10^{-5} Torr. The detailed deposition conditions can be found elsewhere[3-8]. A PZT thin film (100 nm) was deposited on $Pt/SiO_2/Si$ substrate as a seeding layer and was transformed into the perovskite phase at 700°C by RTA. Seeding islands (area: 10×10 μm^2, spaces: 40 and 60 μm) were patterned by conventional lithographic and etching methods. A PZT thin film (200 nm) was then deposited on the substrate having PZT seeding islands.

The growth behavior of the films was investigated using a Nomarski microscope with differential interference contrast. The microstructure and crystal phases of the PZT films were determined using transmission electron microscopy (TEM) and an X-ray diffractometer, respectively.

3. RESULTS AND DISCUSSION

The mechanism for the SNLC process is summarized in Fig. 1. The activation energy for nucleation is generally higher than that for grain-growth. In the case of PZT thin films, the nucleation and grain-growth activation energy were reported to be 441 kJ/mol and 112 kJ/mol, respectively[9]. The SNLC process uses the difference in activation energy between nucleation and grain-growth. The seeded region only requires grain-growth activation energy; however, the other regions need both nucleation and grain-growth activation energy for crystallization. Thus, there exists an activation-energy difference, ΔE, as shown in the figure. Thermal energy should be applied between the value of E_N and E_G for selective growth. It is easily noticed that the higher the energy, the faster the grain-growth. However, the nucleation process occurs statistically, and hence it should be reflected upon the kinetic term in the phase transformation. In the case of the SNLC process, there is a conflict between the growth rate and the selectivity: that is, the higher the temperature, the faster the growth rate. However, there is greater likelihood for undesirable nucleation to occur at sites other than the pre-determined nucleation sites, because of loss of selectivity with temperature[7], as shown in Fig. 2. If high energy were applied for a very short period at only a desired position, while maintaining the other regions of low temperature, undesirable nucleation under conditions for high growth rate could be avoided. We have developed a new annealing apparatus, scanning-rapid thermal annealing

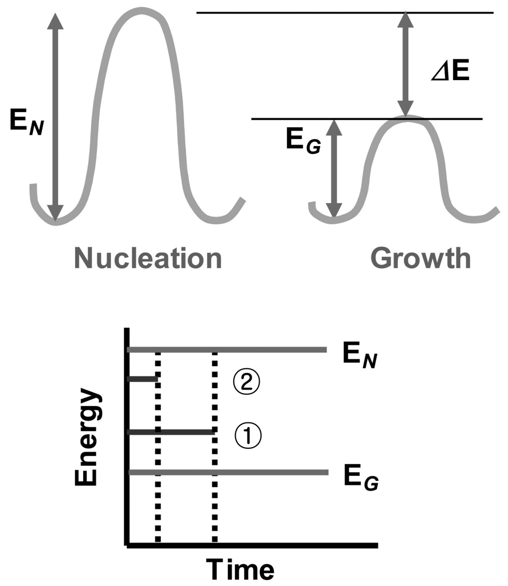

Fig. 1. The SNLC process in PZT thin films. The activation-energy difference between the nucleation and grain growth, ΔE, is the process window for selective grain growth of PZT thin films.

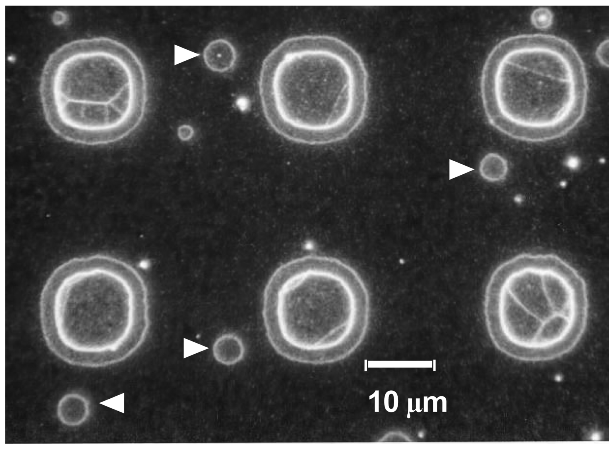

Fig. 2. SNLC of PZT thin films annealed at 580°C for 2 h. The arrows indicate undesirable nucleation at regions other than the pre-determined nucleation sites.

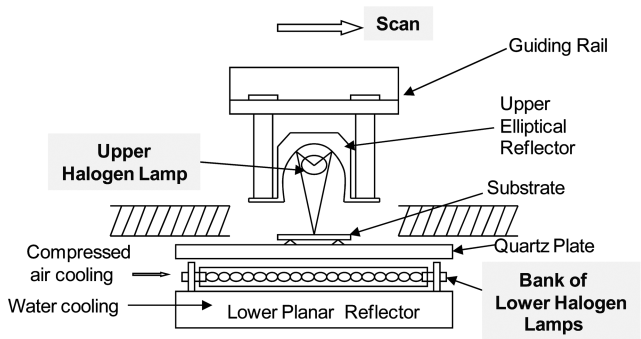

Fig. 3. Scanning rapid thermal annealing apparatus.

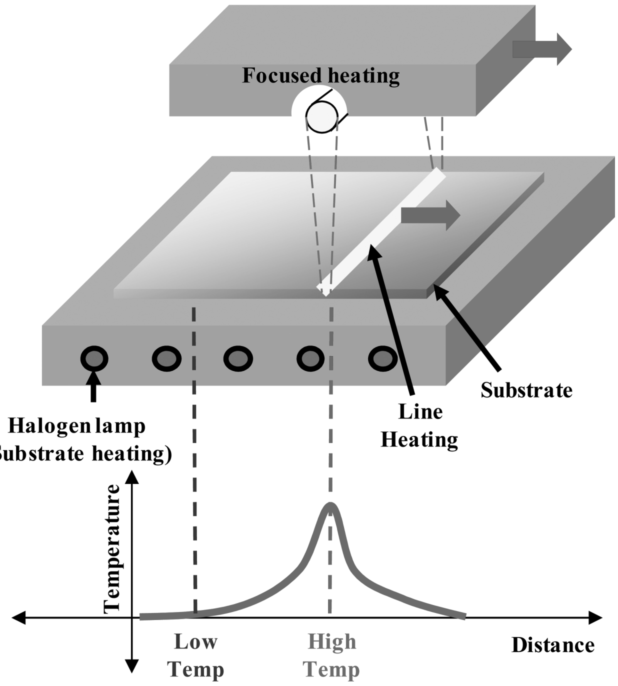

Fig. 4. 3-dimensional illustration of the scanning-RTA apparatus with the schematic temperature profile and scanning direction. (Reused with permission from J.-S. Lee,[8]. Copyright 2007, American Institute of Physics).

(scanning-RTA), for SNLC for this purpose.

SNLC annealing was carried out by scanning-RTA with tungsten-halogen lamps, as shown in Fig. 3. A line-shaped light, which was focused with an elliptical reflector[7], was scanned over a specimen that had been preheated by bottom lamps. The temperature was monitored by a computer-based temperature measurement system using a DT2811 D/A converter (Data Translation, Inc.). Figure 4 shows a 3-dimensional illustration of the scanning-RTA apparatus with the schematic temperature profile and its direction[8]. A local part of the sample was heated at high temperature and the remaining part was maintained at low temperature.

When the upper lamp scanned the sample, the substrate, which was preheated at roughly 500°C, experienced a steep heating and cooling thermal profile. Figure 5(a) shows the measured temperature-time profiles of the scan-RTA processes. It is clear that, in each scanning, the substrate is exposed to the highest temperature for less than 10 s. The major difference between the scan-RTA and conventional RTA is also shown in Fig. 5. The whole area of the sample was exposed to the thermal profile at the same temperature for a desired period in the case of the conventional RTA process, as shown in Fig. 5(b). However, in the scan-RTA case, the temperature profile was very sharp, and thus only

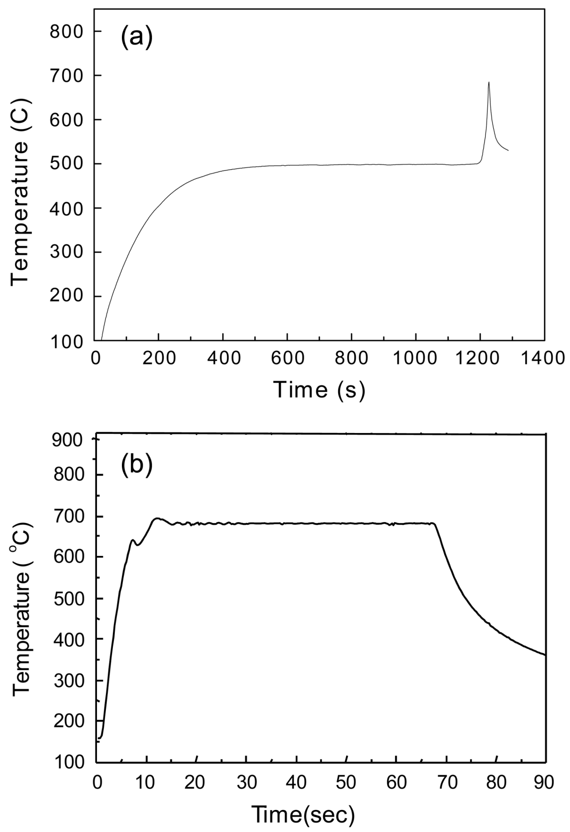

Fig. 5. Typical temperature profiles obtained from scanning-RTA (a) and conventional RTA (b).

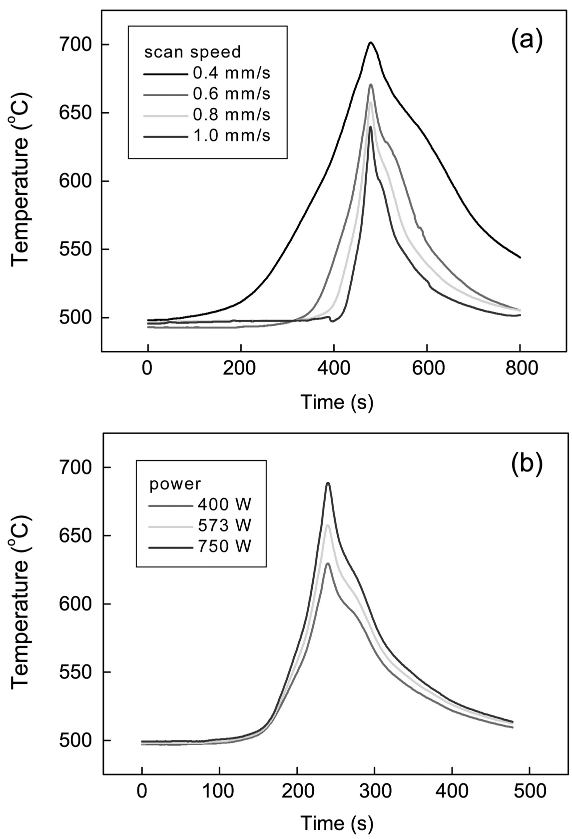

Fig. 6. Temperature profiles during scanning-RTA at different scan speeds (a) and lamp power (b).

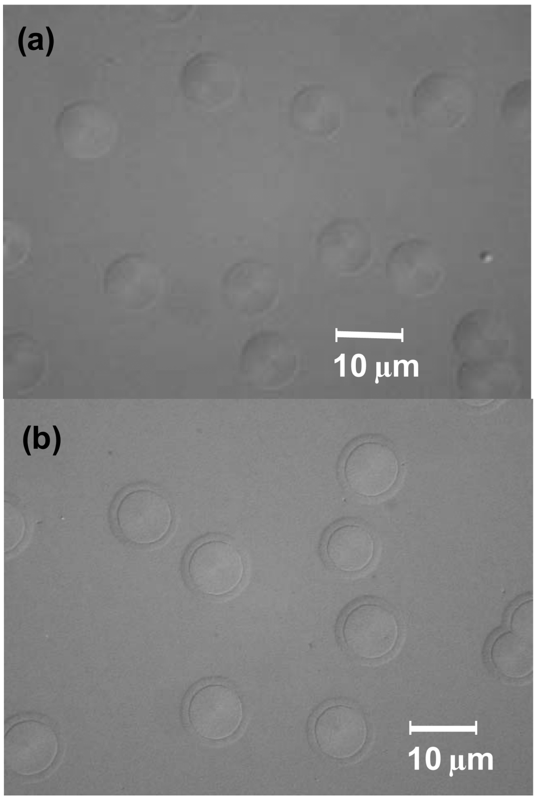

Fig. 7. (a) Partially-crystallized PZT thin films annealed at 680°C for 1 min. (b) SNLC of PZT thin films after scanning-RTA using the temperature profile shown in Fig. 5(a).

the local part of the sample was heated for a short period of time, as shown in Fig. 5(a).

Since the scanning speed and lamp power are adjustable, the thermal profiles can be modified in order to control the annealing process. In Fig. 6(a), it is observed that the annealing temperature profiles become narrower as the scan speed is increased at a constant upper lamp power of 750 W. In Fig. 6(b), it is also found that the peak temperature depends strongly on the lamp power at a constant scan speed of 0.8 mm/s[7]. Therefore, it is possible to adjust the annealing conditions so as to minimize undesirable nucleation and, at the same time, expose the sample to a high temperature for a short period of time.

For the preliminary study, we used partially grain-grown PZT thin films annealed at 680°C for 1 min. The films had an average grain size of 7 μm, as shown in Fig. 7(a). After annealing, the lamp-scan RTA process was carried out. The temperature profile shown in Fig. 5(a) was used. The preheating temperature of the sample was approximately 500°C and the scan speed was 1 mm/s. The peak temperature was 657°C. It was found that grain growth occurred only at the pre-nucleated regions. The lateral growth was 3~4 μm. There was no undesirable nucleation; nucleation only occurred at the pre-nucleated regions, even at the peak

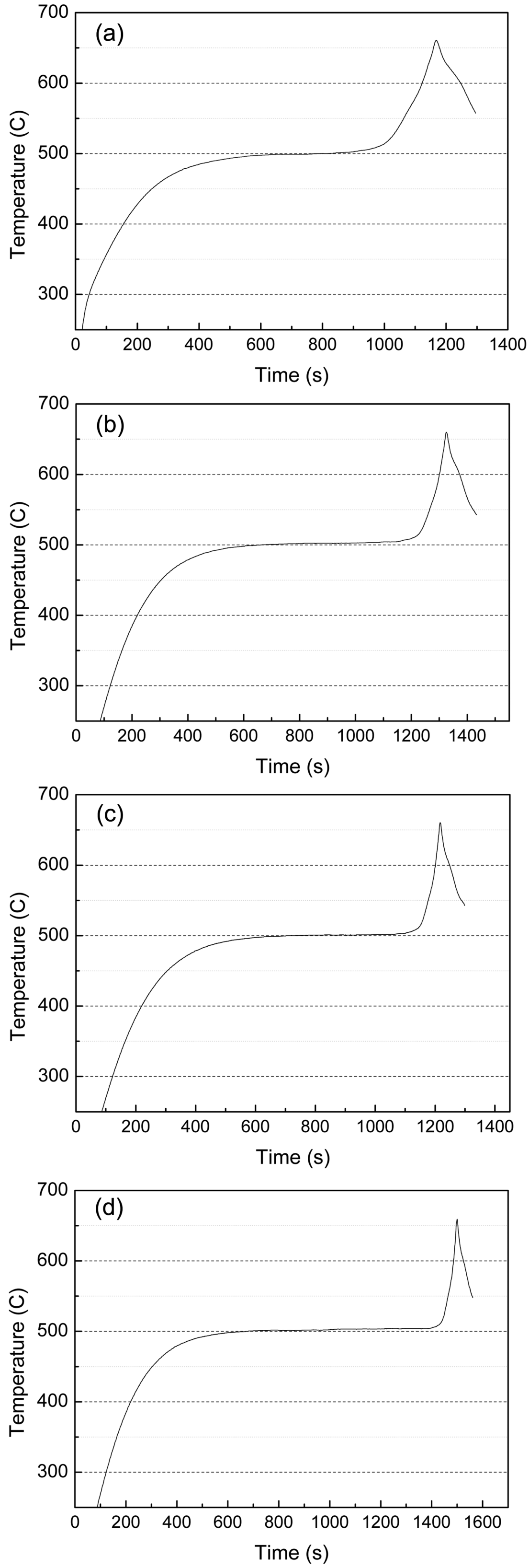

Fig. 8. Temperature profiles with different scanning speeds: (a) 0.5 mm/s, (b) 0.7 mm/s, (c) 0.9 mm/s, and (d) 1 mm/s. Note that the peak temperature was the same for all cases.

temperature of 657°C. (Fig. 7(b)) The annealing temperature could not be increased beyond 620°C in the case of conventional furnace annealing, because of undesirable nucleation. It was found that the growth rate was very fast as compared with that for conventional furnace annealing (~ μm/s vs. ~ μm/h).

The effects of scan speed on the SNLC length were systematically investigated by changing the scan speed while maintaining the peak temperature at 660°C[7]. Thus, the only variable was the scan speed and all other conditions were the same for all samples. The temperature profile used in this experiment is shown in Fig. 8. As easily noticed from the temperature profile, when the scan speed was increased, the temperature increased and then decreased more sharply at the fiducial point of the peak temperature.

Figure 9 shows Normarski micrographs taken with polarized light, illustrating the SNLC of PZT thin films. It is clearly seen that a perovskite phase was grown from the seeds. As the scan speed was decreased from 1 mm/s to 0.5 mm/s, the SNLC length increased from about 4 μm to 20 μm. The dependence of SNLC length on the scan speed is shown in Fig. 9(e). The length sharply decreased with increasing scan speed. The only difference in the annealing conditions was the profile of the scanning temperature. It is postulated that the integral area in the temperature profile plays an important role in the lateral crystallization of PZT thin films. The most important aspect determining the critical temperature; above this temperature the energy transferred from the scanning-RTA to the film overcomes the growth activation energy. By trial and error, the critical temperature was found to be 600°C. This means that growth occurs when annealing is carried out above 600°C. However, in general, nucleation activation energy also exists, and thus it is impossible to grow grains without using the SNLC method at such temperature. Figure 9(e) shows the depen-

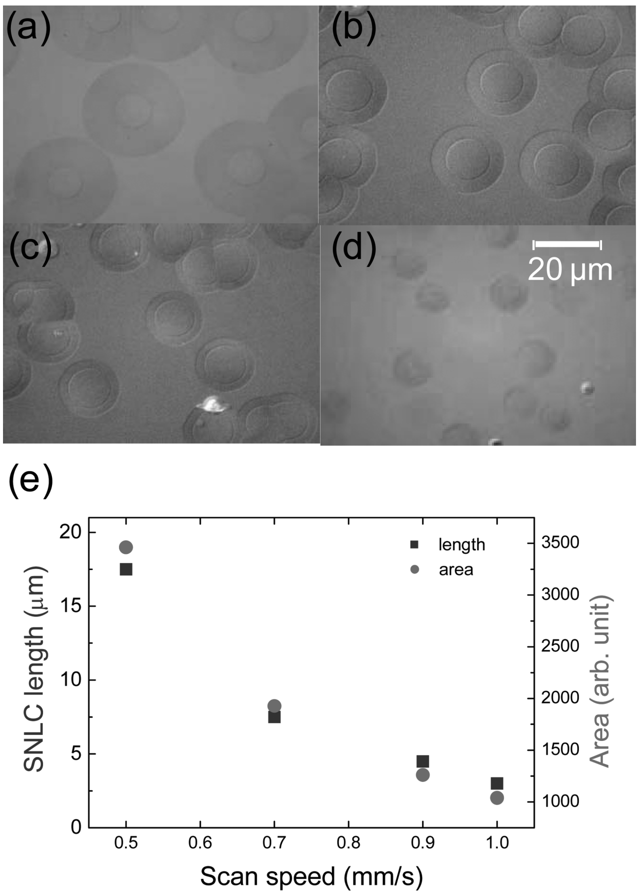

Fig. 9. SNLC of PZT thin films using partially-grown grains as seeds with scan speeds of (a) 0.5 mm/s, (b) 0.7 mm/s, (c) 0.9 mm/s, and (d) 1.0 mm/s. The dependence of SNLC length and the integral area of temperature profiles above 600°C on the scan speed (e). (Reused with permission from J.-S. Lee,[8]. Copyright 2007, American Institute of Physics).

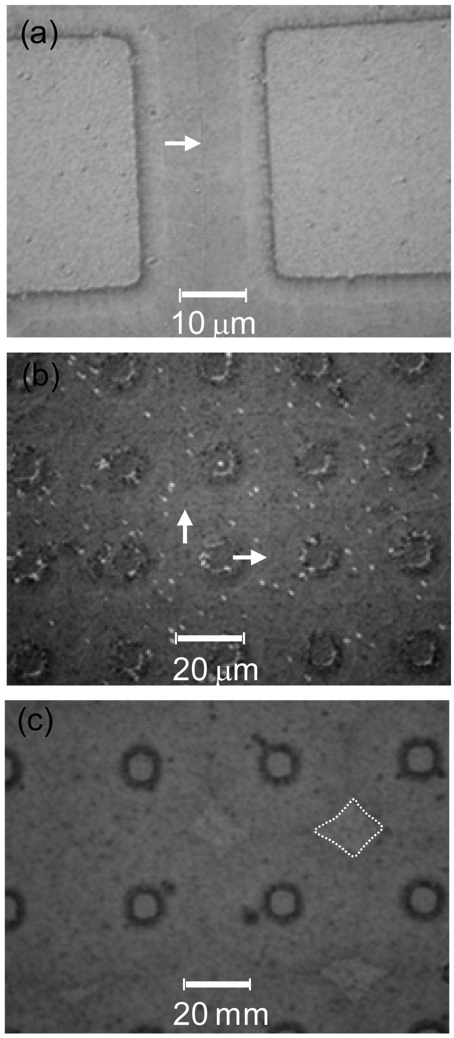

Fig. 10. (a) SNLC of PZT thin films using PZT seeding method. (b) Completion of SNLC. Arrays of single-grain PZT thin films with a square grain-boundary can be observed. The distance between adjacent seeds is 40 μm (b) and 60 μm (c). (Reused with permission from J.-S. Lee,[8]. Copyright 2007, American Institute of Physics).

dence of SNLC length, as well as the integral area of the temperature profile above 600°C, on the scan speed. SNLC lengths as well as integral areas tend to decrease according to the scan speed. The postulate that there exists a critical temperature above which grain growth occurs is also experimentally verified. Furthermore, the integral area above the critical temperature is the energy for grain growth[8].

From the preliminary study using partially grain-grown PZT thin films, the scanning-RTA process was found to be a feasible and effective method for SNLC annealing. Thus, SNLC was carried out using the PZT seed method by scanning-RTA. The temperature profile shown in Fig. 8(a) was used at a scan speed of 0.5 mm/s. Figure 10(a) shows the completion of SNLC. Lateral crystallization began from the PZT seed edge and the perovskite phase finally grew to form a line boundary (indicated by an arrow). The final length was about 20 μm. The maximum length obtained from conventional annealing was about 15 μm by cumulative annealing for 2 h at 580°C and 2 h at 600°C. At annealing temperatures higher than 620°C, random nucleation occurred and consequently large grains could not be obtained due to the absence of a seeding effect. The process time for scanning-RTA was calculated on the basis of the specimen length/scan speed. In this case, the process time was only 51 s. SNLC with small seed size (10×10 μm^2) is shown in Fig. 10(b). The square pattern of single-grained PZT thin films can be clearly seen. Figure 10(c) shows SNLC of PZT with a seed distance of 60 μm. The laterally grown length was 25 μm, keeping the shape of the seed. The crystallization was not completed and the non-crystallized region displayed a lozenge shape[8].

This scan-RTA process has many advantages over conventional furnace annealing or an RTA process; in particular, it offers selective growth, high growth rate, and the potential for a continuous manufacturing process. In this study, an upper lamp was scanned over the specimen to crystallize the samples. However, if the heating source is fixed and the specimens are delivered by a conveyer belt, this method could feasibly be applied in industrial mass production.

4. CONCLUSION

Large single-grained PZT thin films could be obtained using the perovskite PZT seeding method. We demonstrated that the grain boundary location in PZT films could be controlled by controlling the seed location and temperature. In this paper, we presented a mechanism for SNLC, based on an investigation of the phase-transformation kinetics in PZT thin films. From this study on the nucleation and grain-growth process in PZT thin films, we developed a scanning-RTA process and applied it to SNLC. Annealing of SNLC was carried out by scanning-RTA with a tungsten-halogen lamp and thermal profiles could be controlled by changing the scan speed and lamp power. SNLC is affected by scanning conditions, such as scan speed and lamp power, viz. temperature profile. It was found that scanning-RTA is a feasible and effective method for SNLC in terms of reducing process time, preventing undesirable nucleation sites at regions other than pre-determined positions, and in turn increasing the growth rate.

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