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Effect of annealing temperature on ferroelectric electron emission of sol–gel PZT films

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Abstract

In this work, the influence of annealing temperature on the ferroelectric electron emission behaviors of 1.3-μm-thick sol–gel $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) thin film emitters was investigated. The results revealed that the PZT films were crack-free in perovskite structure with columnar-like grains. Increasing annealing temperature led to the growth of the grains with improved ferroelectric and dielectric properties. The remnant polarization increased slightly from 35.3 to 39.6 μC/cm^2 and the coercive field decreased from the 56.4 to 54.6 kV/cm with increasing annealing temperature from 600 to 700 °C. The PZT film emitters exhibited remarkable ferroelectric electron emission behaviors at the threshold voltage above 95 V. The film annealed at 700 °C showed a relatively lower threshold voltage and higher emission current, which is related to the improved ferroelectric and dielectric properties at higher annealing temperature. The highest emission current achieved in this work was around 25 mA at the trigger voltage of 160 V.

Keywords: A. Sol–gel; D. PZT film; Pulse emission

1. Introduction

Since the discovery of strong electron emission from ferroelectric material at CERN [1,2], ferroelectric electron emission has become important in the past decades due to its potential applications in vacuum microelectronics, flat panel displays, and ferroelectric plasma sources [3]. Strong electron emission of up to 100 A/cm^2 was reported from bulk ferroelectric materials under high driven pulse voltage, usually at relatively low vacuum condition. To meet the requirement of technological development for miniaturization, there is great need to lower the threshold voltage with the high emission current by reducing the thickness from millimeter to micrometer level. However, there were only very few works on film emitters reported [4–7] in the last two decades. Compared to the bulk ferroelectric ceramic emitter, PZT films demonstrate very weak electron emission of several nanoamperes to hundreds of microampere current [8,9]. PNZT thin film cathode is another example reported with emission current density of up to 10 μA/cm^2 with switching voltage of up to 22 V and intermittent emission current of up to 20 mA/cm^2 under higher switching voltage [7]. In this work, the influence of annealing temperature on ferroelectric electron emission characteristics of sol–gel PZT films was studied.

2. Experimental

$PbZr_{0.52}Ti_{0.48}O_3$ (PZT) films were prepared using the conventional sol–gel process and spin-coated on $Pt/TiO_2/SiO_2/Si$ wafers [10]. The coated films were dried at 200 °C and pyrolyzed at 350 °C for 2 min, and finally the films were rapid-annealed at temperature from 600 to 700 °C for 3 min. This process was repeated to achieve a final thickness

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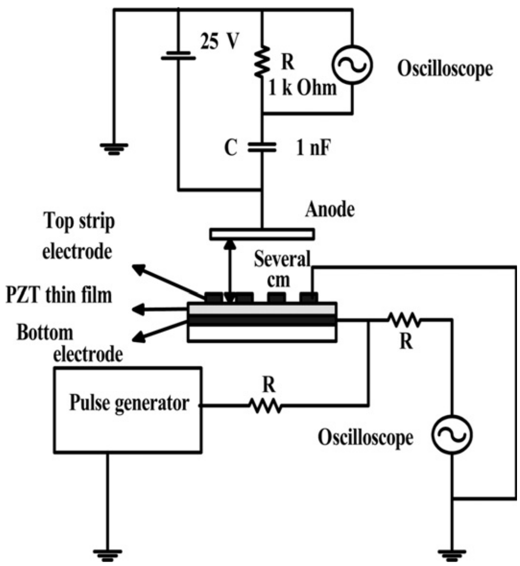

Fig. 1. Schematic diagram of the measurement setup.

of around 1.3 μm. Film thickness was measured by Veeco Dektak 6M stylus profiler. Pt/Ti top electrode was deposited with RF sputtering and with stripe patterned by the lift-off process. Each strip is of dimension 3 mm by 200 μm with spacing of 200 μm between each other within an area of 6.43 mm^2. All the strips were connected with each other and voltage was applied through a pad.

The crystal structure of the films was studied by the Rigaku D/Max-2400 X-ray diffractometer (XRD) equipped with Cu Kα radiation source. Surface morphologies were characterized by the Veeco Nanoscope atomic force microscope (AFM) and the JEOL JSM-7000F scanning electron microscope (SEM) respectively. Dielectric properties were measured by an Agilent 4294A precision impedance analyzer. The *P–E* hysteresis loops were determined by a Radiant WS0603-242 precision work-station with a HVI0702-228 precision high voltage interface.

The electron emission characteristics of PZT films were investigated using a home designed characterization system as illustrated schematically in Fig. 1 [11]. The emission current was converted to voltage signal via a 1 kΩ resistor R in series with a capacitor C. A two-channel Tektronix TDS 460 digital real-time oscilloscope with a 500-MHz bandwidth was used to measure the voltage signals of the emission current and the driven voltage. The pulse generator with impedance 50 Ω was used to generate a high-voltage unipolar pulse with a fast rising time of 1 ns for a duration of 950 ns. All studies were performed in a vacuum of 10^{-3} Torr [12] at room temperature.

3. Results and discussion

3.1. Structural characterization

The crystal structure of 1.3-μm-thick sol–gel PZT films annealed at different temperatures was evaluated using XRD

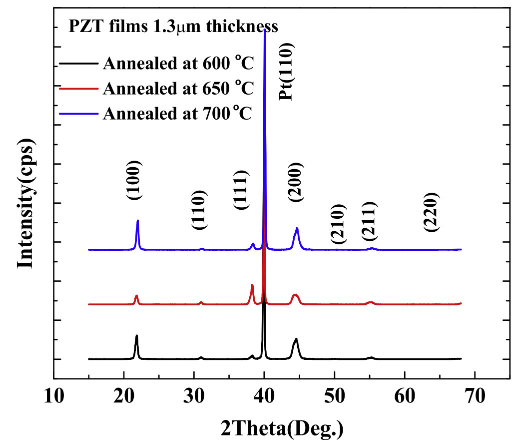

Fig. 2. XRD of PZT film annealed at different temperatures.

measurements. As shown in Fig. 2, the films are composed of pure perovskite grains with the featured diffraction pattern. Correspondingly, the surface morphology of the films was observed using AFM shown in Fig. 3(a). It was observed that by increasing the annealing temperature from 600 to 700 °C the grain size grew from very small size to 300 nm in the PZT films. The SEM cross-sectional microstructure of PZT films at different annealing temperatures shown in Fig. 3(b) indicates that all the films are of columnar-like structure. Sample annealed at 600 °C is smoother than that annealed at high temperature of 650 and 700 °C.

3.2. Electrical characterization

Fig. 4 illustrates the dielectric constant and the loss tangent of the annealed films in the frequency range of 1 kHz to 1 MHz. The results indicate that dielectric constant increases from 1024 to 1350 with increasing annealing temperature without significant change in dielectric loss. The increase in dielectric constant might relate to the grain growth at higher annealing temperature. The *P–E* loops for the films are not shown due to the page limit constraint. However, the films showed well-shaped hysteresis loops with the remnant polarization slightly increased from 35.3 to 39.6 μC/cm^2 and coercive field decreased from 56.4 to 54.6 kV/cm with increasing annealing temperature from 600 to 700 °C.

3.3. Electron emission current measurements

Fig. 5 illustrates a typical trace of emission current and trigger voltage of PZT films annealed at 600 °C. It was observed that all the emissions occurred at the end of trigger pulse similar to the previous published results [6]. The voltage drop during the rising time of the applied pulse was due to the high capacitance of the ferroelectric films. It was observed that fast rising pulse was required for ferroelectric electron emission. In comparison, a slow rising pulse with a time span of hundreds of microsecond was performed and eventually there was no electron

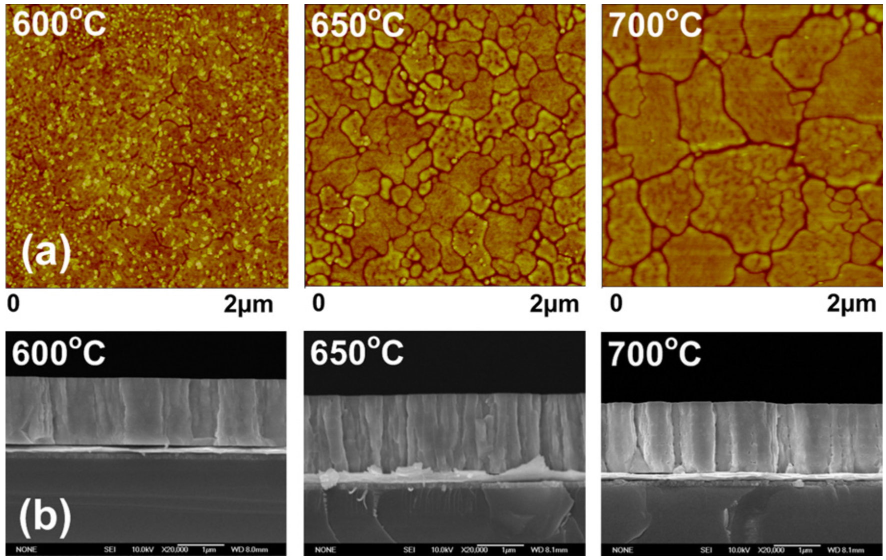

Fig. 3. AFM (a) and cross-sectional SEM (b) images of 1.3-μm-thick PZT films annealed at different temperatures.

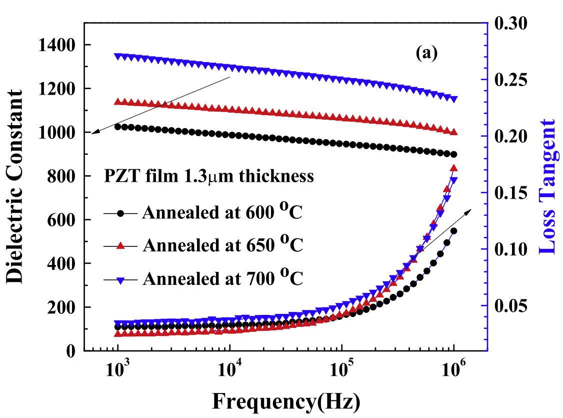

Fig. 4. Dielectric constant of 1.3-μm-thick PZT films annealed at different temperatures.

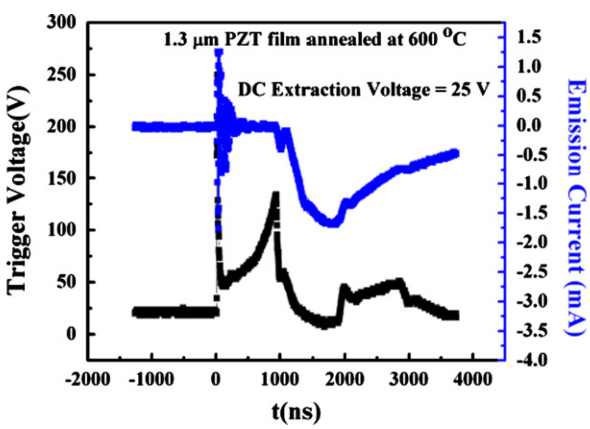

Fig. 5. PZT films traces of trigger voltage and emission current of PZT films annealed at 600 °C.

emission detected. It is because the electron emission can only occur if the spontaneous polarization is induced by the polarization deviation with fast heat, laser, electric field pulses or mechanical pressure, on a submicrosecond time scale [13].

The electron emission characteristics of sol–gel PZT films were investigated by changing the trigger voltage and dc extraction voltage as shown in Fig. 6. In the plots of electron emission current versus trigger voltage under extraction voltage of 25 V, it is shown that above the threshold voltage, increasing trigger voltage led to the increase of emission current and finally it saturates at a certain level. It might be related to the polarization deviation process around the edge of the top electrode driven by the stray electric field. The surface polarization deviation started to occur above the threshold field that might be related to the domain switching and finally the emission current saturates while the saturation polarization has achieved. The films annealed at 700 °C has a response of lower threshold voltage and higher emission current as compare to other films annealed at 600 and 650 °C. As mentioned above high annealing temperature resulted in the increase of dielectric constant and remnant polarization in the films, and the low coercive field. Fig. 6(b) showed the effect of dc extraction voltage on the emission current of the films driven by the trigger voltage of 160 V. A dc extraction voltage was applied to the anode plate as an acceleration potential for extracting the electrons from ferroelectric thin film cathodes. It is observed that emission current increase linearly by increasing the dc extraction voltage.

4. Conclusion

In this work, 1.3-μm-thick sol–gel PZT thin film emitters annealed at different temperatures were prepared onto $Pt/TiO_2/SiO_2/Si$ wafer for ferroelectric electron emission applications. The results revealed that the formed perovskite structure films are crack-free with columnar structure.

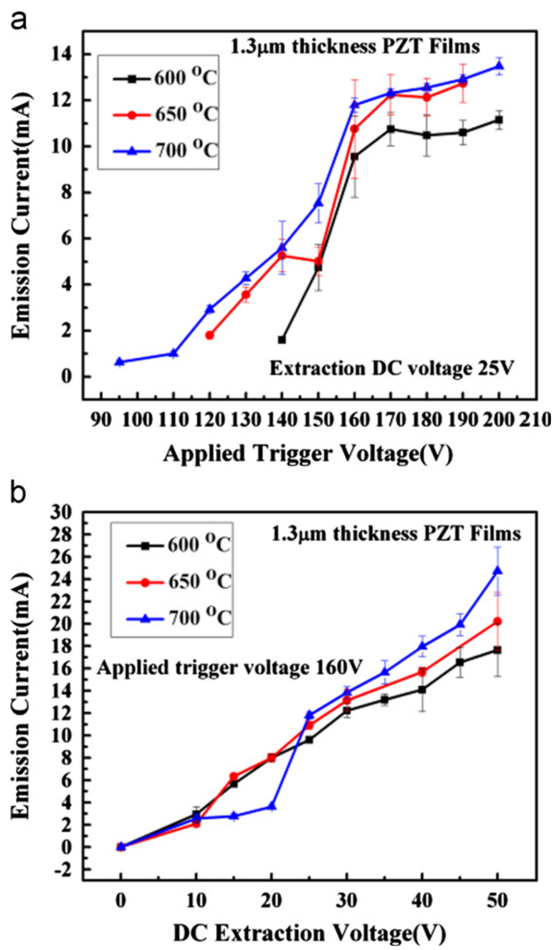

Fig. 6. PZT films traces of trigger voltage and emission current of the films annealed at different temperatures.

Increasing annealing temperature led to the growth of the grains with improved ferroelectric and dielectric properties. The films showed well-shaped hysteresis loops with the remnant polarization slightly increased from 35.3 to 39.6 μC/cm^2 and coercive field decreased from the 56.4 to 54.6 kV/cm with increasing annealing temperature from 600 to 700 °C. Correspondingly the dielectric constant increased from 1024 to 1350 with increasing annealing temperature without significant change in dielectric loss. The PZT film emitters exhibited the remarkable ferroelectric electron emission behaviors at the threshold voltage above 95 V. The film annealed at 700 °C has a response of lower threshold voltage and higher emission current as compared to other films annealed at 600 and 650 °C, which is related to the improved ferroelectric and dielectric properties at higher annealing temperature. The highest emission current achieved in this work was around 25 mA at the trigger voltage of 160 V.

Acknowledgments

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