出國報告（出國類別：國際會議）

2013第二屆機械工程及材料國際研討會 (2013 2nd International Conference on Mechanical Engineering and Materials)

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摘要

2013第二屆機械工程及材料國際研討會(2013 2nd International Conference on Mechanical Engineering and Materials)是在中國海南島三亞市舉行,日期從1月27日到28日。我是搭乘中華航空公司的直航班機，於1/26離開台灣到達三亞，1/29回到台灣，整個過程蠻輕鬆愉快的，不用長時間搭飛機及調時差。我的海報安排在1/27上午，題目為“PZT Thin Films Deposited by RF Magnetron Sputtering”，這是利用磁控濺鍍來製作壓電薄膜，論文主要探討製程參數對壓電特性的影響，如濺鍍氣氛中氬氣和氧氣的比例、退火的溫度及退火的時間，我們並以x光繞射儀、原子力顯微鏡、掃描式電子顯微鏡來量測壓電薄膜的特性，結果顯示加入更多氧氣有助於提升壓電品質，最佳的退火溫度約在700度。研討會過程遇到各國學者，包含多位台灣學者，互相交流學術心得。這是我第三次參加中國大陸舉辦的國際研討會。之前常參加歐洲地區的研討會，但是機票貴、搭機時間長、要調時差，覺得還蠻辛苦的。參加中國大陸的研討會，就不會有這些問題，感覺還蠻輕鬆愉快。不管到達當地或者回來台灣，可以立即投入工作，不用調時差，不用因長時間搭機需要額外休息。比較起來，應該儘量參加亞洲方面的研討會。

目次

一、 **目的**

這次發表的論文是有關壓電材料的製作及測試，利用磁控濺鍍來製作壓電薄膜，主要是探討製程參數對壓電特性的影響，並建議最佳的製程參數。這是我們有興趣自行進行的研究，並沒申請國科會補助或是廠商合作，因此我們利用節餘款來補助，也希望能將計畫的結果至少發表在國際研討會，因此我們決定參加這個國際研討會，接受更多人的檢驗，以提升計畫的品質。這個研討會的性質是屬於所有機械領域，也適合我們的計畫，所以希望能和相近領域的專家互相交流及討論。我的題目為“PZT Thin Films Deposited by RF Magnetron Sputtering”，這是利用磁控濺鍍來製作壓電薄膜，論文主要探討製程參數對壓電特性的影響，如濺鍍氣氛中氬氣和氧氣的比例、退火的溫度及退火的時間，我們並以x光繞射儀、原子力顯微鏡、掃描式電子顯微鏡來量測壓電薄膜的特性，結果顯示加入更多氧氣有助於提升壓電品質，最佳的退火溫度約在700度。

二、 **過程**

為了節省轉機的時間，我訂購華航從桃園直飛三亞的飛機，但飛機的班次有限，也就是停留在三亞最少的時間是從1/26飛到三亞，1/29飛回台灣。1/26下午3:20從桃園機場飛到三亞已是晚上6點左右，自行搭公車到會議的旅館已是7點多。在公車上認識同樣從台灣來開會的學生，高慶揚博士生，目前正在台大土木系就讀，同時也是聯華電子公司的廠務工程處處長，看起來年紀和我差不多。飯店(三亞麗景酒店)的位置和公車站牌還有些距離，花了一些時間才到達飯店。我們住的飯店就是會議所在地，如圖1，接下來就不用舟車勞累。1/27日早上去報到後，如圖2，即參與兩場的Plenary speeches。第一場是由Prof. Jun Wang, Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong主講“Advances in Neural Network Approaches to Nonlinear and Robust Model Predictive Control”。類神經網路(neutral network)可以用來對任何系統建立輸入和輸出之間的模型，不用去推導該系統的物理模型及數學公式，純粹使用簡單的神經元的概念及簡單的數學關連公式，就可以來建立預測模型，非常有吸引力。不過這個方法的挑戰在於如何以最少的訓練資料來建立預測模型，並得到很好的預測值，尤其在非線性系統更是困難。Prof. Wang針對控制系統如何建立類神經網路模型，有深入淺出的介紹，並給出一些實務的建議。在會場上，我也遇到一位台灣的學者，我們在這部份也互相交流一些經驗。

第二場是偏環保方面，由中國方面的教授Prof. Yijin Wu, 主題為“The impact of Climate Change on Agriculture”。這是有關溫室效應如何影響農業生產的演講，演講人以精美的圖片及有說服力的數據，來呈現及證明溫室效應及其對農業的影響，讓我覺得我們應努力降低溫室效應。中間休息時間10:20到11:00即為Poster session。我這次是參加Poster session，如圖3，在Poster session和我合影的即為高慶揚處長。針對我的主題，我們是選用pt為下電極，有其他學者建議可以考慮以ITO為下電極，這部份我們也已完成探討，只是沒有收錄在這篇論

文中。有些對我們實驗的細節很有興趣，一直詢問一些實驗過程的問題，如厚度如何量測、粗糙度如何量測、鐵電特性如何量測，我皆詳細告知。當然也有人對鐵電特性的結果有所質疑，這部份我們確實不敢百分百確認結果的重複性，是真的需要更多試片的重複驗證，才能很有信心的確認結果。也有學者介紹他們利用藍寶石為下電極的結果，很有啟發性。

下午和1/28日早上皆為Oral session。高慶揚處長即在下午進行口頭報告。我就盡量選一些研究領域較相關的口頭報告來聽，如“Experimental Investigations on the Mixed-mode Essential Fracture Work of PC/ABS Alloy”是利用實驗來探討PC/ABS混合材料介面的混合破壞模式，並建立其混合模式破壞的準則。“Deformation and Failure Processes of Sheet Metal Drawing of Circular Cup-shape Parts”是探討板材成形為圓形杯的過程中，其變形及破壞的情形，這篇主要在模擬分析。“Strong, Stiff and Tough Graphene Papers Made from Ultralarge Graphene Oxide Sheets” 是利用graphene 薄層來疊層製造成graphene紙張，利用實驗量測來證明此紙張具有高強度、高勁度、及高韌度。“Research of Crack Non-contiguous Interface Simulation Method Based on Meshless Weight Function Arguments Modification”是一篇模擬分析的論文，利用無網格有限元素法的方式來建立加權函數，並用於模擬分析裂縫介面的情形。“Development and Performance of Thermoset Green Composites Reinforced by Unidirectional Abaca Fiber”, 這篇是實驗探討單方向abaca纖維來製造熱固型複合材料，這種複合材料是屬於綠色科技。論文中探討製程參數對複合材料品質的影響，品質上是以材料的強度、勁度及破壞韌度等來評估。這些是聽過且比較有印象的。有些論文是關於破壞分析及實驗，有些論文是關於複合材料的特性探討，還有些是有關於無網格有限元素在破壞方面的計算。由於這個研討會的論文範圍比較廣，所以也有些論文是偏向環境保護方面，就沒有去參加。

這次研討會，可能參加的人比較少，所以是和另一個研討會合併，這個研討會為2013 2nd International Conference on Future Communication, Computing, Control and Management (ICF4C 2013)。因此，在Oral session是由兩個研討會的參與者上台報告，並沒有分開進行，所以有些報告者的研究領域和我的興趣差異較大，比較無法進入問題互動。整個研討會是在1/28日的中午結束。在會場也遇到國立嘉義大學機械與能源系的林肇民教授及南開科技大學電機資訊學院院長江昭龍教授。會議飯店(三亞麗景酒店)位在大東海灣的附近，1/28日下午即到沙灘上走一走。1/29日我搭公車到三亞市區及亞龍灣的沙灘走一走。當日下午7:05分搭飛機，可惜飛機並沒有準時起飛，約晚了1小時，所以回到桃園機場已是晚上10點多，趕快搭高鐵到台中，幸好還能順利接上火車回到斗六。回到家已是晚上12點多。

三、 心得

這是我第三次參加中國大陸舉辦的國際研討會。之前常參加歐洲地區的研討會，但是機票貴、搭機時間長、要調時差，覺得還蠻辛苦的。參加中國大陸

的研討會，就不會有這些問題，感覺還蠻輕鬆愉快。不管到達當地或者回來台灣，可以立即投入工作，不用調時差，不用因長時間搭機需要額外休息。比較起來，應該儘量參加亞洲方面的研討會。

我覺得主辦單位應該可以在許多細節方面做得更好，如事前的連絡、研討會議程等方面，都是可以再改進的。

另外，我覺得近幾年在中國大陸有很多國際研討會，其主辦單皆是香港的文教機構，其研討會的品質並不高，往後應該要避免參加。

圖1研討會的告示牌

圖2黃順發於會場

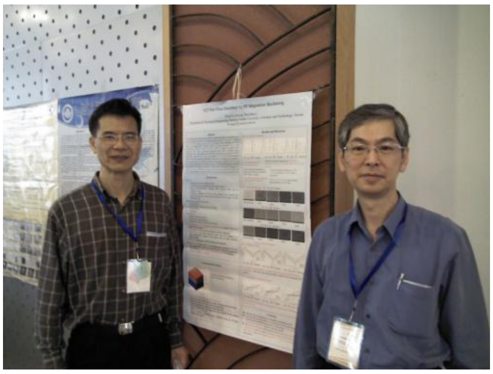

圖3高慶揚處長與黃順發於論文海報前

四、 **建議事項**

無。

五、 **(附錄)**

PZT Thin Films Deposited by RF Magnetron Sputtering

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Keywords: PZT thin film; RF sputtering; perovskite; leakage current; ferroelectric property.

Abstract. PZT thin film was fabricated by using RF-sputtering process, and platinum was used as bottom electrodes. The sputtering gases were Ar：O_2＝25：0 sccm, Ar：O_2＝20：5 sccm, or Ar：O_2＝15：10 sccm. After sputtering, the PZT film was annealed for 5 minutes under O_2 gas environment and at the temperature of 600 ^{0}C, 650 ^{0}C, 700 ^{0}C or 750 ^{0}C. To judge the quality of the deposited PZT film, its physical properties and electric properties were evaluated. The results indicate that the best crystallization temperature of PZT thin film is about 700 ^{0}C. Also, the roughness of the PZT thin film becomes larger with the increasing of annealing temperature. By adding more oxygen in the sputtering gas, one could have better crystallization of the PZT film. As for the electrical properties, the leakage current of PZT thin film increases with the increasing of annealing temperature. Furthermore, the ferroelectric property is affected by the crystallization amount of perovskite, the thickness of PZT thin film, and the diffusion situation between the bottom electrode and the PZT film.

Introduction

Lead zirconate titanate (Pb(Zr,Ti)O_3 or PZT) has been a well-known ferroelectric and piezoelectric material because of its high electromechanical coupling, short response time, and low actuation voltage. PZT thin films have attracted great attention as promising candidates for use in micro actuator [1], micro sensors [2], non-volatile ferroelectric random access memory devices [3], surface acoustic wave filters [4], etc.

To create PZT thin films, various methods have been used, such as sol-gel process [5], metal-organic chemical vapor deposition [6], laser ablation [7, 8], and sputtering [9]. Among these methods, sputtering is likely to be a dominant method because of its simple fabrication process, low processing temperatures, and possible integration with silicon technology. However, sputtering deposition methods requires a post-annealing treatment to crystallize the film in the perovskite phase.

Radio-frequency (RF) magnetron sputtering with stoichiometric single oxide target on silicon substrate is a popular method to sputter PZT thin films. During this process, Pt/Ti bilayers are commonly used as a bottom electrode for PZT films [10-11]. Platinum (Pt) has been selected mainly due to its stability in a high temperature oxygen environment and its high Schottky barrier height. However, platinum has poor adhesion to a substrate such as silicon dioxide. Hence, a titanium (Ti) interlayer is used to improve the adhesion. The purpose of this work is to investigate the properties of PZT thin films deposited on platinum electrode by RF magnetron sputtering with different process parameters.

Experimental Procedure

The substrate chosen was a 4-inch p-type (100) silicon wafer. It was cleaned by a RCA cleaning processes before use. Then it was put into a high temperature chamber to grow a layer of SiO_2 with 100 nm thickness to protect the platinum electrode from the silicon substrate. After that, titanium and platinum films was deposited by a dual electron gun evaporation system. The titanium film was used to increase the adhesion of the platinum film on the SiO_2 layer, and the platinum film was used as the bottom electrode. The sputtering of PZT thin films was carried out under a base pressure of 2.6x10^{-6} torr at 100 W RF power. The working pressure was 8 mtorr and the gas flow rates of argon and oxygen were Ar：O_2＝25：0 sccm, Ar：O_2＝20：5 sccm, or Ar：O_2＝15：10 sccm. The deposition time was 100 minutes. Since the PZT thin films right after deposition are amorphous, a post-annealing treatment is necessary to crystallize the film in the perovskite phase. To discuss the effect of annealing temperature, 600 ^{0}C, 650 ^{0}C, 700 ^{0}C or 750 ^{0}C was used in the rapid thermal annealing for 5 minutes under pure oxygen condition. After that, silver top electrodes with a diameter of 200 μm and 500 μm, , as shown in Fig. 1, were deposited on the PZT films by a lift-off process for measuring the electrical properties. To characterize the deposited PZT thin films, 3D Alpha-Step Profilometer was used to measure their thickness, SEM was used to see their surface morphology, and XRD was applied to judge their lattice structure. For the electrical properties, the leakage current was measured with respect to the applied voltage by an LCR meter. The ferroelectric properties were obtained using an RT-66A standard test system.

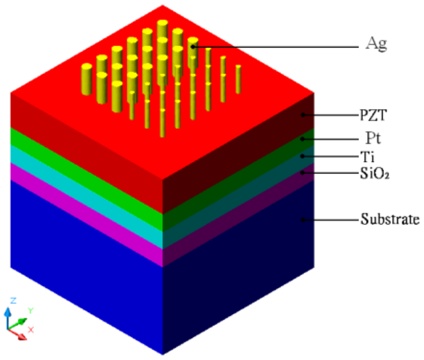
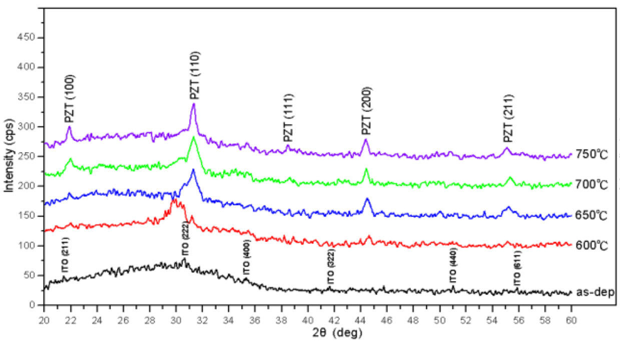
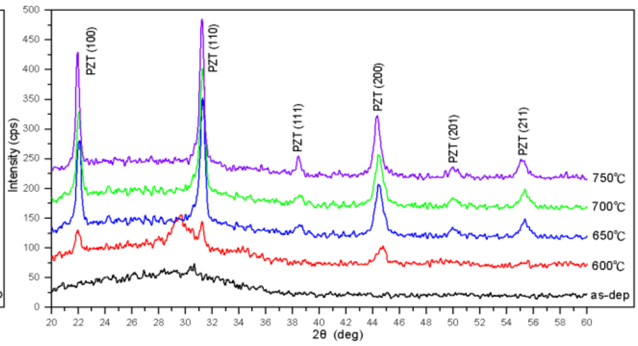


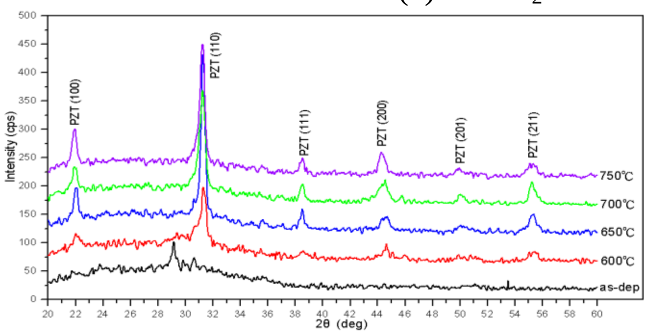
Fig. 1 Schematic diagram of PZT specimen



(a) Ar：O_2＝25：0 sccm



(b) Ar：O_2＝20：5 sccm

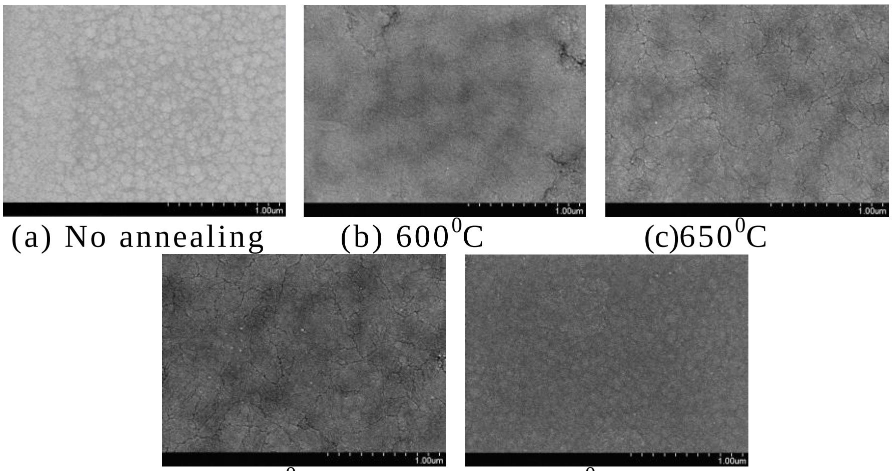


(c) Ar：O_2＝15：10 sccm

Fig. 2 XRD pattern of deposited PZT film under different gas flow rates

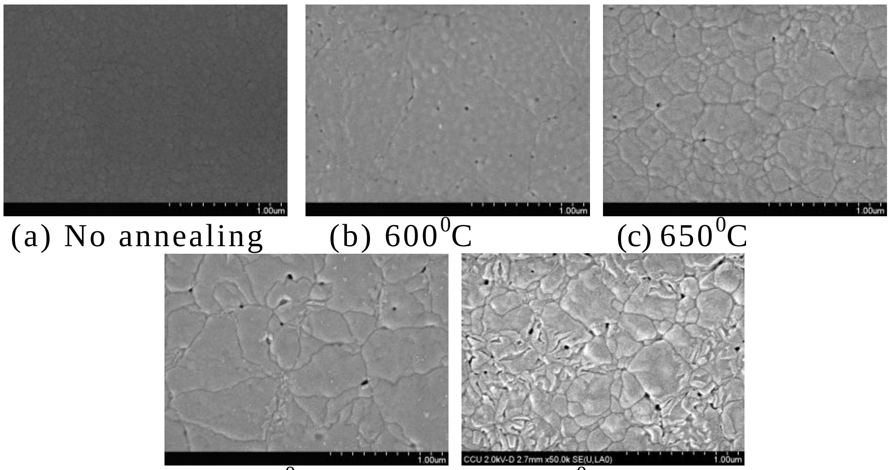
Results and Discussion

Crystallization of PZT Films. The X-ray diffraction patterns of the deposited PZT films under the gas flow rates of Ar：O_2＝25：0 sccm are shown in Fig. 2(a) for different annealing temperatures. As shown, when there is no annealing treatment, there is no clear appearing of perovskite phase. When the annealing temperature is 600 ^{0}C , PZT(100), PZT(110), PZT(111), PZT(200), and PZT(211) start to occur. As the annealing temperature is further increased, the crystallinity of PZT films is clearer. However, if the annealing temperature is 750 ^{0}C, the crystallinity of PZT films is decreased. Hence, the suitable annealing temperature is between 650 ^{0}C and 700 ^{0}C. As shown in Figs. 2(b) and 2(c) for the gas flow rates of Ar：O_2＝20：5 sccm, and Ar：O_2＝15：10 sccm, respectively, the crystallinity of PZT film is increased as compared to that in Fig. 2(a) at the same annealing temperature. This implies that high oxygen flow rates may increase the crystallinity of PZT films.


(a) No annealing (b) 600^{0}C (c)650^{0}C

(d) 700^{0}C (e) 750^{0}C

Fig. 3 Surface morphology of deposited PZT film under the gas flow rates of Ar：O_2＝25：0 sccm


(a) No annealing (b) 600^{0}C (c) 650^{0}C

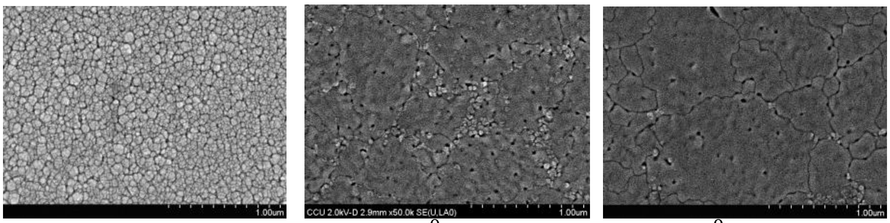
(d) 700^{0}C (e) 750^{0}C

Fig. 4 Surface morphology of deposited PZT film under the gas flow rates of Ar：O_2＝20：5 sccm

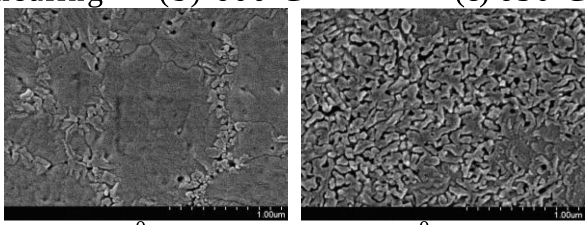
Surface Morphology. The surface morphologies of the deposited PZT films under the gas flow rates of Ar：O_2＝25：0 sccm are shown in Fig. 3 for different annealing temperatures. Without annealing treatment, the surface is quite flat and it should be under amorphous structure. As the annealing temperature is increased, the crystalline becomes clearer. However, when the annealing temperature is 650 ^{0}C, some cracks along the grain boundary appear. But, these cracks disappears as the annealing temperature is 750 ^{0}C. As the gas flow rate is Ar：O_2＝20：5 sccm, the crystalline and cracks become clearer as the increasing of the annealing temperature as shown in Fig. 4. When the gas flow rate is Ar：O_2＝15：10 sccm, similar phenomenon occurs as shown in Fig. 5. In comparison, the surface cracks become less in the latter gas flow rate.

As for the surface roughness measured by atomic force microscope, the root-meant-square (RMS) roughness of the deposited PZT films becomes larger with the increasing of annealing temperature.

For example, when the gas flow rate is Ar：O_2＝20：5 sccm, the RMS value is 1.5 nm without annealing treatment. It becomes 4 nm, 10 nm, 18 nm, and 23 nm, as the annealing temperature is 600 ^{0}C, 650 ^{0}C, 700 ^{0}C and 750 ^{0}C, respectively. This may come from the crystallinity of the film. As for the thickness of the deposited PZT film, the average thickness measured by Alpha-step is about 500 nm, 330 nm, and 260 nm for the gas flow rate of Ar：O_2＝25：0 sccm, 20：5 sccm, and 15：10 sccm, respectively. Since argon is used to bomb the target for PZT deposition, the thickness of the deposited PZT film is decreased as the decreasing of the argon.

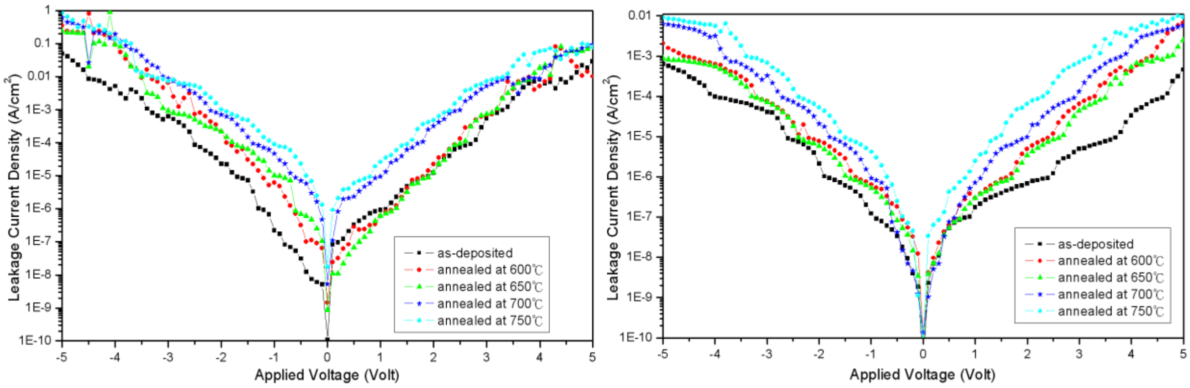


(a) No annealing (b) 600^{0}C (c) 650^{0}C

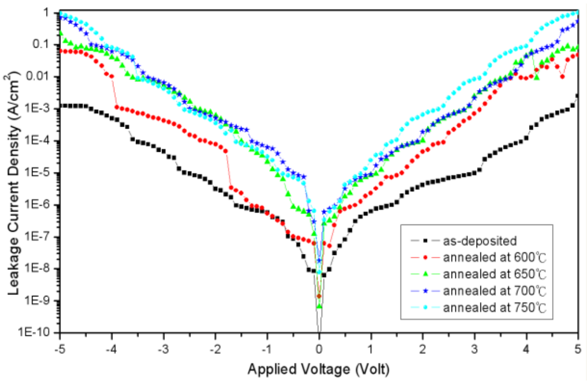


(d) 700^{0}C (e) 750^{0}C

Fig. 5 Surface morphology of deposited PZT film under the gas flow rates of Ar：O_2＝15：10 sccm



(a) Ar：O_2＝25：0 sccm (b) Ar：O_2＝20：5 sccm



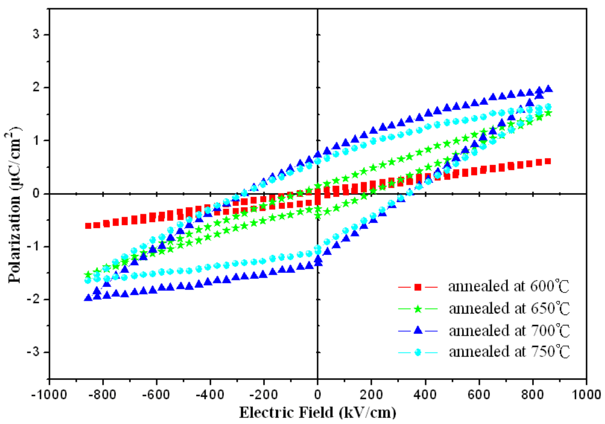
(c) Ar：O_2＝15：10 sccm

Fig. 6 Leakage current density of deposited PZT film under different gas flow rates

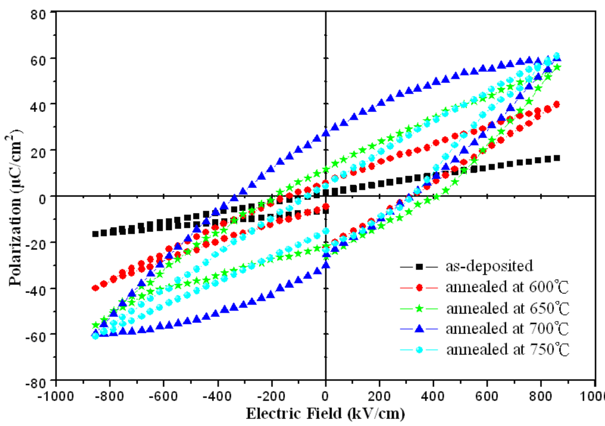
Leakage Current. The leakage current density with respect to the applied voltage is shown in Fig. 6 under different gas flow rates. As shown, the leakage current density increases as the increasing of the annealing temperature. This may come from the cracks created by the evaporation of Pb and O_2.

Among the three gas flow rates, the one with Ar：O_2＝20：5 sccm has the least leakage current density, as shown in Fig. 6(b). This may be due to the balance between the reducing effect of the addition of oxygen and the increasing effect of the grain size. From the viewpoint to have less leakage current, it is recommended to deposit PZT films under the gas flow rate of Ar：O_2＝20：5 sccm and less annealing temperature.

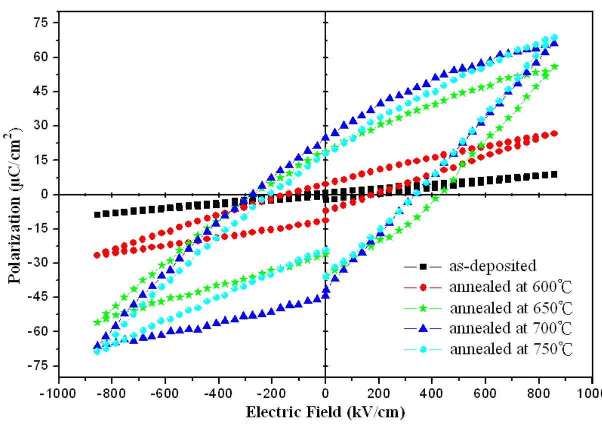
Ferroelectric Hysteresis Curve. The ferroelectric hysteresis curve without the addition of oxygen is shown in Fig. 7. It is clear that the ferroelectric properties are not good. As the gas flow rate is Ar：O_2＝20：5 sccm, the ferroelectric properties is significantly increased as shown in Fig. 7(b). For example, the saturated polarization is 60 μC/cm^2 and the remnant polarization is 27 μC/cm^2 as the annealing temperature is 700 ^{0}C, while the saturated polarization is 61 μC/cm^2 and the remnant polarization is 5 μC/cm^2 as the annealing temperature is 750 ^{0}C. As the gas flow rate is Ar：O_2＝15：10 sccm, the saturated polarization is 66 μC/cm^2 and the remnant polarization is 25 μC/cm^2 as the annealing temperature is 700 ^{0}C, while the saturated polarization is 66 μC/cm^2 and the remnant polarization is 17 μC/cm^2 as the annealing temperature is 750 ^{0}C, as shown in Fig. 7(c). Therefore, it is better to control the gas flow rate from Ar：O_2＝20：5 sccm to Ar：O_2＝15：10 sccm and to anneal the film at 700 ^{0}C.



(a) Ar：O_2＝25：0 sccm



(b) Ar：O_2＝20：5 sccm



(c) Ar：O_2＝15：10 sccm

Fig. 7 Ferroelectric hysteresis curve of deposited PZT film under different gas flow rates

Conclusions

In this work, PZT thin film was fabricated by using RF-sputtering process, and Platinum was used as bottom electrodes. From the above discussion, the addition of oxygen in the gas flow will increase the crysatllinity and ferroelectric properties. However, the leakage current is also increased. To create the perovskite phase, it is necessary to have annealing treatment in the present manufacturing process. Among them, the annealing temperature with 700 ^{0}C may have the best results.

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