鐵電薄膜電滯曲線之新型態量測方法與逐層結晶之金屬/鐵電/絕緣/半導 結構之特性研究

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摘要

在本論文中，鐵電材料的介電特性、元件的應用與電滯曲線的量測方法是探討的主題。為了提供較完整的概念，本文會簡單介紹"鐵電隨機存取記憶體"的基本操作原理及其他的鐵電記憶體的結構與電滯曲線的量測技術。

本論文主要分為兩大部分：

一、MFM、MFIS 結構之製作與特性的探討

二、新型態電滯曲線之量測方法

在第一部份，我們將對在不同氧壓下退火的鋯鈦酸鉛薄膜(PZT)來做特性的比較，並對使用逐層結晶的鉭酸鍶鉍（SBT）所構成的 MFIS 結構的特性來做探討。

在第三章，我們將探討利用低氧壓結晶的鋯鈦酸鉛薄膜的鐵電及介電特性。此鋯鈦酸鉛薄膜（120 nm）採用溶膠凝膠法來製備，沉積在鍍有白金/鈦的矽基板上。我們發現在 500 ^{o}C、低壓環境下結晶的鋯鈦酸鉛薄膜，比起在常壓結晶的薄膜，具有較高的殘存極化量及較低的矯頑電場。而對於在低氧壓（60 mbar）的環境下沉積的薄膜，在 2 V 的操作電壓下，其殘存極化量（$2P_r$）高達 $36\mu C/cm^2$，矯頑電場（$2E_C$）大約 99.9kV/cm。這些改善可能是由於鋯鈦酸鉛薄膜內具適當的氧含量及較少的有機殘存物，因為這些殘存物的減少，可能有助於鈣鈦礦結構的相轉換。而這些氧含量及有機殘存物的減少，可以由歐傑電子顯微鏡的縱深成份分析與熱脫附常壓游離質譜儀來加以確認。此外，這些

在不同氧壓下結晶的薄膜的介電特性及漏電特性也會在此篇論文中被比較。

在第四章，逐層結晶（layer-by-layer-crystallized）的鉭酸鍶鉍（$SrBi_2Ta_2O_9$ (SBT)）薄膜沉積在二氧化鉿（HfO_2）的緩衝層（buffer layer）上的基本特性會被討論。實驗結果顯示出，具有逐層結晶（layer-by-layer-crystallized）的鉭酸鍶鉍（$SrBi_2Ta_2O_9$ (SBT)）薄膜的金屬－鐵電－絕緣－半導（metal-ferroelectric-insulator-semiconductor (MFIS)）結構具有一個鐵電型態的遲滯曲線（ferroelectric hysteresis），且在操作電壓為 6 V 的時候具有大約 0.34 V 記憶區間（memory window）。在一大氣壓、溫度 850 ^{o}C 的氧環境下做後續熱處理，發現逐層結晶（layer-by-layer-crystallized）的金屬－鐵電－絕緣－半導（MFIS）的結構具有優異的耐久特性，且記憶區間（memory window）及電容的儲存時間（capacitance retention time）並沒有衰退。 此結構的儲存時間（retention time）超過 10^4 秒，且其外差預測的時間大約為 10^5 秒。

在第二部份，我們使用了定電流的方法來研究小尺寸鐵電電容的特性，並提出了兩種量測電滯曲線的方法。

在第五章，我們以定電流的方法（constant current method）來研究微小尺寸的鐵電電容的電滯曲線。當鐵電電容的尺寸減小的時候，我們發現探針設備的寄生效應可能會增加小尺寸鐵電電容的最大極化量（maximum polarization）。而定電流的方法（CC method）也可以用來計算探針設備的寄生效應，進而可以得到校正後的電滯曲線。此外，我們也利用電感、電容、電阻分析儀(LCR meter) 來量測小尺寸鐵電電容的介電常數，並且與校正後的電滯曲線中所得的介電常數來做比較。我們也發現，在量測的介電常數與由電滯曲線中求得的介電常數中，具有一個吻合的結果。這些結果顯示出定電流的方法（CC method）可以用來研究小尺寸鐵電電容的鐵電特性。

在第六章，我們提出三角形電流的方法（triangular current method）用來量測鐵電電容的電滯曲線。此方法與定電流的方法（CC method）相似，都是以電流源的方式來獲取電滯曲線。藉由施加三角形充電電流（triangular charging current）到樣品，可獲得一個圓滑、幾乎沒有雜訊的電壓波形。並經由積分公式將充電電流（charging current）轉

換成電荷，得到其相對的電滯曲線。在不同的量測條件之下，那些電滯曲線的相似性顯示出充電電流（charging current）大小及其階數的多寡（number of steps）皆不會影響量測的結果。此外，探針設備的寄生效應也同樣被發現會影響量測的結果，尤其是當鐵電電容尺寸變小的時候。而三角形電流的方法（TC method）也可以用來決定探針設備的寄生電容值的大小，進而可以得到校正過後的小尺寸鐵電電容的電滯曲線。這些結果顯示出三角形電流的方法（TC method）構成了一個新的研究鐵電電容之電滯曲線的方法。

在第七章，電流－電壓量測方法（I-V measurement method）被利用來研究鐵電電容的鐵電特性。藉由使用三角形的電壓波形，可以獲得遲滯的電流特性，經由積分的公式也可得到其相對應的極化－電壓 (P-V)的曲線。此外，兩種預先極化的量測方式（poling measurements）也被用來研究完全調換（full-switching）及非調換（nonswitching）的電流特性。在由極化－電壓 (P-V)的曲線所獲得的非揮發性極化量（nonvolatile polarization）與使用預先極化的量測方式（poling measurements）所獲得到的非揮發性極化量當中，可發現相當好的一致性。此外，一個經修改過後的預先極化的量測方式（poling measurements）也被使用來研究鐵電電容的資料保存持久的特性。在保存期間（retention duration），發現一個動態的調換電流特性（switching current characteristic），且當保存時間（remaining time）增加的時候，也發現在半電滯曲線圖（half-hysteresis loops）中會有一個增加的矯頑電壓（increased coercive voltage）。再者，另外一個修改過的預先極化的量測波形也被使用來研究鐵電薄膜的退極化（depolarization characteristics）特性。

New Methods for Measuring Hysteresis Loops of Ferroelectric Thin Film and Characteristics of Layer-by-Layer Crystallized Metal/Ferroelectric/Insulator/Semiconductor (MFIS) structure

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Abstract

In this thesis, several topics concerning the dielectric properties, device applications, measurement techniques of electrical hysteresis of ferroelectric thin films are studied. The introduction of the ferroelectric and dielectric materials, the basic operations of 1T1C ferroelectric random access memory (FeRAM) and other FeRAM structures are briefly described. The hysteresis measurement techniques of ferroelectric capacitors are also addressed.

This thesis can be divided into two major parts:

(1) the fabrication and characterization of MFM and MFIS structures,

(2) new methods for hysteresis measurement.

In the first part, the oxygen pressure effect of properties of PZT thin film and characteristics of layer-by-layer crystallized Pt/$SrBi_2Ta_2O_9$/HfO_2/Si structure are studied.

In chapter 3, we focused on the ferroelectric and dielectric properties of low-pressure crystallized PZT thin films deposited on the Pt/Ti/SiO_2/Si substrate, as described in chapter 2. The properties of sol-gel derived 120-nm $PbZr_{0.52}Ti_{0.48}O_3$ thin films crystallized in low-pressure O_2 ambient at a low temperature of 500°C have been investigated. It is found

that $PbZr_{0.52}Ti_{0.48}O_3$ films crystallized in low-pressure O_2 ambient depict higher remanent polarization as well as lower coercive field, compared to those annealed in O_2 atmospheric pressure. The remanent polarization (i.e., $2P_r$) for samples annealed in 60 mbar O_2 ambient is as high as 36μC/cm^2, and the coercive field ($2E_C$) is 99.9kV/cm at an applied voltage of 2 V. The improvement by the low-pressure oxygen annealing is ascribed to less incorporation of residues and adapted oxygen content in the resultant $PbZr_{0.52}Ti_{0.48}O_3$ films, since the reductions of these residual species are beneficial for the complete transformation of perovskite structure. The reductions of oxygen content and other residues such as CO_2, H_2O are confirmed by Auger depth profiles and thermal desorption spectra (TDS), respectively. Moreover, the dielectric and electrical properties of these films are also compared.

In chapter 4, the basic characteristics of layer-by-layer-crystallized $SrBi_2Ta_2O_9$ (SBT) films deposited on a 14-nm-thick HfO_2 buffer layer are discussed in chapter 6. Experimental results indicate that the metal-ferroelectric-insulator-semiconductor (MFIS) stack with a layer-by- layer-crystallized SBT film exhibits ferroelectric hysteresis and a memory window of around 0.34 V at an operating voltage of 6.0 V. When post deposition annealing was performed at 850 ^{o}C, the layer-by-layer-crystallized MFIS structure exhibited favorable switching characteristics with negligible degradations of the memory window and the capacitance retention time. The retention time of this structure exceeded 10^4 s and the extrapolated time was about 10^5 s.

In the second part, constant current method is used to determine the electrical hysteresis of small-sized ferroelectric capacitor. Besides, two methods are proposed to perform the electrical hysteresis measurement.

In chapter 5, a constant current method (CCM) is introduced to directly measure the electrical hysteresis of micron-sized $Pb(Zr,Ti)O_3$ capacitors prepared on $Pt/Ta/SiO_2/Si$ substrates, as described in the chapter 3. The parasitic effect of the probing setup is found to possibly increase the maximum polarization as the capacitor's area is reduced. The CCM technique can be exploited to calculate the parasitic capacitance of the probe station and then easily construct the corrected hysteresis loops. Additionally, the dielectric constants of small capacitors were measured using an LCR meter, for comparison with the linear dielectric constant obtained from the high-field slope of the hysteresis loops with parasitic correction. Strong agreement was found between the measured dielectric constants and the results obtained from the hysteresis loops. These results indicate that the CCM technique represents an approach for investigating the ferroelectric characteristics of small ferroelectric capacitors.

In chapter 6, a triangular current (TC) method is proposed in this thesis to measure the hysteresis loops of $Pb(Zr,Ti)O_3$ capacitors, as described in chapter 4. Like the constant current (CC) method, this method is a current source mode method for obtaining hysteresis loops. By applying a triangular charging current to a specimen, a measured voltage profile, which is almost noiseless and smooth in the high-field region, is obtained and its hysteresis curve can be determined using integral calculus to convert the charging current to charge. Under various charging conditions, the similarity of the obtained hysteresis curves implies that the step charging current and number of steps do not affect the measured results. Moreover, the parasitic effect of the probe setup is found to possibly increase the maximum polarization of the ferroelectric capacitor as the area of the capacitor is reduced. The TC method can be utilized to determine the parasitic capacitance of the probe setup and then can easily determine the corrected hysteresis loops of small capacitors. These findings reveal that the TC method constitutes a new method for measuring the hysteresis loops of ferroelectric capacitors.

In chapter 7, the current-voltage (I-V) measurement method is utilized to investigate the ferroelectric characteristics of ferroelectric capacitors, such as hysteresis loops, switching current characteristics, retention properties and depolarization characteristics. By applying triangular voltage wave forms without sweeping and measuring delay, the hysteresis switching current characteristic was determined and the polarization-voltage (P-V) loop could

be obtained using an integral calculus. Additionally, two kinds of poling measurement were utilized to investigate the full-switching and nonswitching current characteristics. A strong agreement was found between nonvolatile polarization (ΔP) obtained from P-V loops and that obtained by poling measurements. Moreover, modified poling measurements were utilized to study the retention property of ferroelectric capacitors. A dynamic switching current characteristic was found in retention duration and an increased coercive voltage was also observed in its half-hysteresis loops as remaining time increased. Furthermore, another modified poling profile was utilized to investigate the depolarization characteristics of ferroelectric films.