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論文内容要旨

The focus of the research presented in this dissertation is concentrated on understanding the relationship between the internal (residual) stress and preferred orientation of PZT thin films based upon the analysis of lattice mismatching variation, and furthermore, the influence of such factors as internal (residual) stress and preferred orientation on ferroelectric thin-film properties by adopting several aspects of the PZT preparation process, including by Sol-Gel method deposited directly on the Pre-annealed $Pt/Ti/SiO_2/Si$ substrate, Sol-Gel method with PEG addition, and *in-situ* Pulsed Laser Deposition (PLD) process on the Sol-Gel derived highly (111)-oriented epitaxial seed layer.

Chapter 1. Introduction

Investigation of ferroelectric and piezoelectric properties of ferroelectric films in highly preferred orientation is not only of fundamental interest, but also critical to their applications for non-volatile ferroelectric memories (Nv-FeRAM) and for microsensors, microactuators used in micro-electro-mechanical systems (MEMS). Thin ferroelectric films have higher energy densities, larger strain capabilities, and more rapid response times than their bulk counterparts. Among the many families of ferroelectrics, perovskite $PbZr_xTi_{(1-x)}O_3$ (PZT) thin films near the morphotropic boundary (MPB) with $x \approx 0.52$ are most attractive owing to their high dielectric constants, high spontaneous polarization, and high electromechanical coupling factor. Unlike bulk ferroelectrics, PZT films develop large residual stresses and preferred crystallographic orientation during processing. In order to optimize performance and improve the application properties, it is essential to understand the factors that may influence the properties of ferroelectric thin films. The present work investigates the internal (residual) stress and preferred crystallographic orientation effects on the dielectric and ferroelectric properties of PZT thin films from several aspects of experimental result and analysis, through which the relationship between the internal (residual) stress and preferred crystallographic orientation of PZT films has been clarified by analyzing the "epitaxial" lattice mismatching degree of PZT (111) // Pt (111).

The spontaneous polarization and saturation polarization of PZT films intensively depend on the preferential orientation. The saturation polarization and spontaneous polarization of the (111) oriented PZT films are much better than the (100) oriented ones, which features superior ferroelectric switching properties. Since that ferroelectric thin films have different electric properties and microstructure (e.g. column-like grains) from their bulk counterparts, a more reliable and convenient method of obtaining the highly (111)-oriented "epitaxial" PZT thin film on Pt (111) substrate directly is primarily desirable with respect to much better electric properties. Herein, the techniques used for fabricating highly (111) preferred orientation and reasonably thick PZT films have been of special interest.

In this aspect, some conventional techniques such as screen-printing ink and jet print deposition have been utilized to fabricate thick and large-area PZT films. However, the electrical properties of the obtained films by these ways are far from the maximal values on account of the porous microstructure and the not well aligned orientations of polycrystalline films. So, it is critical to develop some techniques that enable us to obtain PZT films in highly (111) preferred orientations, or unanimous oriented or even epitaxial on platinized silicon wafers so that those ferroelectric and piezoelectric properties of PZT films can be well improved.

As for the available techniques for fabricating PZT films, it is noticed that Sol-Gel process provides the advantages of being able to obtaining PZT films with good quality and being able to control the preferred orientations by adjusting the pyrolysis temperature. However, due to the limitation of critical thickness of a single layer, it takes more than 20 repetitions (over 30 hrs.) of coating and firing procedure to obtain the PZT films of 3-μm thickness. This repeating process is time-consuming and brings up the risk of contamination and interdiffusion between the PZT layer and the bottom electrodes, and furthermore the formation of apparent cracks due to the accumulated internal tensile stress in PZT layers during the deposition process.

Based on such a unfavorable situation, some kind of stress releasing agent-PEG (a *Polyethylene Glycol, a stress relaxing organic molecular polymer)* is needed to add in the PZT precursor solution in order to suppress the crack formation and obtain the nearly highly (111) PZT thick and crack-free films.

On the other hand, it is well recognized that the PLD offers high deposition rate (1-3 μm / hour) which makes it attractive for fabricating thickness films. However, the electrical properties of the PZT films prepared by PLD are inferior to those of the films derived by Sol-Gel due to the necessary higher annealing temperature in PLD in comparison with Sol-Gel process (750 °C vs. 600 °C) which results in the impurity of crystalline phases (remnant nonferroelectric pyrochlore phase). Another factor responsible for the deteriorated properties is attributed to the random orientations in PLD derived PZT films. Hence, in order to improve the electrical properties of the PZT films, it is required that the processing temperature for crystallizing as-deposited PZT films should be lowered and the orientations in PZT films should be aligned.

Taking the above facts into account, it was naturally deduced that it would be rewarding to integrate PLD and Sol-Gel methods in such a way that the merits of these two methods can be utilized while the demerits of them should be avoided.

So, in order to prepare PZT films with precise Zr/Ti ratios near MPB, a Sol-Gel processing is often employed primarily due to its chemical homogeneity and facility of stoichiometric control compared with other fabrication techniques. However, the texture control for polycrystalline PZT films on conventional Pt (111)/Ti/SiO_2/Si substrates in a Sol-Gel processing is of great challenge because that most of the methods used in the previous studies are sensitive to temperature or dependent on other deposition conditions, and sometimes require expensive vacuum possessing procedures. In order to overcome such disadvantages and obtain highly (111)-oriented PZT thin films as well, several aspects of the PZT preparation process, including Sol-Gel method directly on the Pre-annealed Pt/Ti/SiO_2/Si substrate, Sol-Gel method with PEG addition, and *in-situ* Pulsed Laser Deposition (PLD) process on the Sol-Gel derived highly (111)-oriented epitaxial seed layer have been adopted, which PZT thin film was deposited directly on the Pre-annealed Pt/Ti/SiO_2/Si substrate first by Sol-Gel method. Through such series of experiments the highly (111)-oriented both PZT thin film and thick film have been attempted to fabricate by eliminating the unfavorable factors such as intrinsic residual stress and microstructure defects existing in Pt substrate before PZT deposition so that the dominant "epitaxial" relationship between PZT (111) // Pt (111) should be maintained in maximum degree during the PZT deposition process throughout the whole film interface.

The purpose of the current research was to develop an easy and convenient process for preparing highly (111)-oriented PZT films as an effort to realize the applications for both PZT thin films in FeRAM and thick ones in MEMS devices, and furthermore, to elucidate the process of Pre-annealing of Pt/Ti/SiO_2/Si substrate and its effect on the internal stress state and preferred orientation of PZT films by using different fabrication methods, such as single Sol-Gel method, Sol-Gel method with PEG addition, or *in situ* growth of PLD deposition on Sol-Gel derived highly-(111) oriented epitaxial seed layer.

In order to confine the extent of this research suitable for a dissertation, the main objectives in the research are given in the following:

1. To investigate the fabrication of highly (111) Sol-Gel derived PZT films deposited on Pre-annealed $Pt/Ti/SiO_2/Si$ substrates as a foundation for analysis on the relationship between (111) preferred orientation PZT thin films and lattice mismatching situation with Pt substrates induced by internal stress variation corresponding to the thermal treatment process.
2. To investigate the effect of PEG addition on the preferred orientation, microstructures and electric properties of PZT thin films deposited on the Pre-annealed $Pt/Ti/SiO_2/Si$ substrates for analysis on the relationship between highly (111) preferred orientation PZT thin films and lattice mismatching situation with Pt substrates induced by releasing of internal tensile stress further corresponding to the thermal treatment process and different amount of PEG addition.
3. To investigate the fabrication of thick PZT films in highly (111) preferred orientation through *in-situ* PLD growth on Sol-Gel derived seed layer, and furthermore to discuss the effect of substrate temperature on preparation of PZT films by pulsed-laser deposition in order to obtain much better ferroelectric thick films.

Chapter 2. Preparation of highly (111)-oriented PZT thin films by Pre-annealing of $Pt/Ti/SiO_2/Si$ substrate

Initially, PZT thin films with a Zr/Ti ratio of 52/48 were deposited by the Sol-Gel technique directly onto platinized silicon wafers which had been employed Pre-annealing treatment. The relationship between the crystallographic orientation and internal (residual) stress was analyzed according to the lattice mismatching of PZT (111) // Pt (111) in different internal stress states. The total residual stress in the polycrystalline film consists of intrinsic, thermal, and extrinsic contributions. Among them, the thermal stress is emphatically important resulting from the thermal expansion coefficient (TEC) mismatch for a highly (111)-oriented polycrystalline film on a cubic substrate. The residual stress in the PZT (52/48) film upon cooling from the crystallization temperature was tensile and temperature dependent. The calculated residual stress in the bottom Platinum electrode was also tensile and had a much higher value than the residual stress in the PZT film. In addition, the experimental values of tensile residual stress were greater than the numerical calculations. These discrepancies indicate that thermal expansion mismatch between the film and substrate accounts for only major part of the residual stress induced in the film during processing. Other factors such as solution evaporation in the Sol-Gel technique, grain formation, grain interaction, and phase transformation, which are categorized into intrinsic stress, also should be taken into account in order to predict accurately the residual stress in the film induced during processing. For Sol-Gel derived PZT thin film, such an intrinsic stress is inevitable due to its processing characteristic; while for Pt substrate, through the Pre-annealing process, the intrinsic stress in bottom Platinum electrode formed during the process of sputtering deposition can be eliminated so that the lattice parameters of Pt (111) could vary in linearity with respect to the thermal stress, which would not be interfered by the uncertain intrinsic stress any more. Thus, a favorable epitaxial lattice matching for PZT (111) // Pt (111) has been preferred to adopting growth of PZT thin film in <111> orientation. Compared with other growth orientation such as <100> or <110> in competition, the <111> has been largely promoted to a preferred orientation predominately

Chapter 3. Effect of PEG addition on the preferred orientation of PZT thin films deposited on Pre-annealed $Pt/Ti/SiO_2/Si$ substrate

Furthermore, the effect of PEG addition on the preferred orientation, microstructure and electric properties of PZT thin films deposited on the Pre-annealed Pt substrates in order to explore the feasibility on fabrication of highly (111)-oriented and crack-free PZT thick films by PEG addition was investigated. Through comparison with the PZT thin films deposited on the Pt substrates without Pre-annealing, the relationship between lattice mismatching degree and preferred orientation under different internal stress states was testified and elucidated further.

This research shows that The large internal residual stress can not changed the lattice mismatching apparently and PZT films still keep (111) orientation after the Pre-annealing of $Pt/Ti/SiO_2/Si$ substrate, which still maintains a favorable lattice matching of Pt (111) // PZT(111) even after the stress relaxation in PZT film by PEG addition. In addition, the relaxation of tensile stress during the heating process doesn't account for the formation of less (111) preferred orientation of PZT film by changing lattice mismatching degree after PEG addition.

Chapter 4. Deposition of (111)-oriented PZT films by PLD on Sol-Gel derived seed layer

Finally, a thin PZT film was spin-coated on the Pre-annealed Pt/Ti/SiO_2/Si substrate by Sol-Gel as seed layers prior to *in-situ* PLD method was used to prepare the PZT film. Crystalline phases and preferred orientation in the PZT films were investigated by X-ray diffraction analysis and their electrical properties were evaluated by measuring their *P-E* hysteresis loops and dielectric constants. A better solid-phase (111) epitaxial effect between the PZT film and the seed layer can reduce the activation energy for crystallization, and therefore contributes to lower the annealing temperature for crystallization and to control the preferred orientation of the PZT film, as observed in chapter 4 and proved by the XRD results in the current chapter.

Based on these results, the effect of seed layer in lowering the crystallization temperature and controlling the preferred orientation of PZT films by PLD was evaluated. In addition, the effect of substrate temperature on the crystallization structure, microstructure and electrical properties of *In-situ* growth PZT thin films by PLD process, has been discussed.

This research shows that under the condition of same (111) preferred orientation in PZT thin films, the denser and more homogeneous microstructure, much better ferroelectric and dielectric properties can be obtained.

Chapter 5. Conclusions and remarks for future work

The conclusions for the current research and some remarks for the future related work are summarized in this chapter.

The main conclusions of this study can be outlined as follows:

1. Highly (111)-oriented PZT thin film can be fabricated and controlled by adopting the Pre-annealing of Pt/Ti/SiO_2/Si substrate, in which the internal stress has been changed largely in Pt substrate that makes a more favorable PZT(111)//Pt(111) lattice matching.
2. Different amount of PEG addition can not change the (111) preferred orientation of PZT thin films deposited on the Pre-annealed Pt/Ti/SiO_2/Si substrate, and then (111)-oriented thick PZT films can be fabricated through Sol-Gel method with PEG addition and then obtained superior electric properties.
3. With increasing of the substrate temperature during the *in-situ* growth of PLD process on highly (111)-oriented Sol-Gel derived PZT seed layer, the microstructure and electric properties of PZT films deposited have been greatly improved.
4. This research shows that epitaxial growth of PZT films by *in-situ* PLD process on highly (111)-oriented seed layer is more efficiently practical for preparing relatively thick PZT films in (111) preferred orientation for MEMS device applications than other methods.

It has been proved that the analysis on the preferred orientation of PZT thin film deposited directly on Pt substrate in the view point of epitaxial lattice matching mechanism combined with internal (residual) stress variation is practical and effective. The variation of internal (residual) stress induced by thermal processboth in PZT thin film and Pt substrate corresponding to the whole deposition process could not change epitaxial lattice matching of PZT (111) // Pt (111) at all, resulting in nearly the same (111) lattice mismatching degree between PZT thin film and Pt substrate, which is only interfered by the unreleased intrinsic stress as sputtered condition, unexpected stress induced by the interaction Pt-Ti stacking layer, or microstructure defects.

論文審査結果の要旨

チタン酸ジルコン酸鉛（$Pb(Zr_xTi_{1-x})O_3$、PZTと略記）の電気的特性と圧電特性は結晶方位に依存するため、優れた電気的特性と圧電特性を有するPZT薄膜を得るには、薄膜の結晶配向を制御する必要がある。Sol-gel 法により PZT 薄膜を作製する際、薄膜の結晶配向は先駆体溶液の化学組成と溶媒、加熱プロセス（熱分解加熱温度と加熱速度）と基板材料等に依存する。通常に使われる $Pt/Ti/SiO_2/Si$ 基板の場合、熱分解温度により PZT 薄膜の結晶配向を (111) 面にある程度は制御できるが、再現性が高くなく配向性も低い。そこで、本研究では Sol-gel 法で高い(111)配向を有する PZT 薄膜を再現性良く作製することを目的として、PZT 薄膜の結晶配向に及ぼす $Pt/Ti/SiO_2/Si$ 基板のプレアニーリングと先駆体溶液への応力緩和剤 Polyethylene glycol (PEG) の添加の影響を検討した。さらに、一層の Sol-gel 法の(111)配向を有する PZT 膜をシードレーヤーとして、その上に Pulsed Laser Deposition (PLD)法により PZT 薄膜を作製し、薄膜の結晶構造、結晶配向、微細組織と電気的特性に及ぼす基板加熱温度の影響についても調べた。

論文は全編5章で構成されている。

第1章は序論であり、本研究の背景および目的を述べている。

第2章では、Sol-gel法のPZT薄膜の結晶配向に及ぼす$Pt/Ti/SiO_2/Si$基板のプレアニーリングの影響について調べた結果、600℃-30 minのプレアニーリングでPZT薄膜の結晶配向が(111)面に確実に高い配向性で制御できることが明らかになった。その理由としては、基板のプレアニーリングにより下部電極Pt/Ti膜は内部応力が緩和されると同時に組織的に回復し、PZT/Pt界面ではミスフィットの小さい界面構造（PZT(111)//Pt(111)、PZT(110)//Pt(220)）がPZTの<111>優先成長を効率的に働くようになるためと考えられる。

第 3 章では、第 2 章で検討した(111)配向を有する PZT 薄膜の作製方法に対する先駆体溶液への PEG 添加の影響について調べた。その結果、PEG 添加量の増加とともに PZT 薄膜の(111)面の結晶配向の割合が下がるが、PEG 添加量が 15%以下の場合、(111)面の結晶配向の割合 を 80% 以上に維持できることが明らかになった。

第 4 章では、第 2 章で検討した(111)配向を有する PZT 薄膜の作製方法で、まず $Pt/Ti/SiO_2/Si$ 基板上に厚さ 0.1 μm のシードレーヤーをコーティングし、その上に PLD 法で厚さ 1 μm 以上の PZT 薄膜を作製し、基板加熱温度の結晶構造、結晶配向と微細組織に及ぼす影響について調べた。その結果、基板温度の増加と共に、PZT 薄膜は緻密になり、電気的特性が大幅に向上することが明らかになった。これは、基板温度の増加と共に基板に付着した原子やイオン等の運動エネルギーが高くなり、ペロブスカイト相への結晶化過程における原子やイオン等の再配列が容易になるためと考えられる。

第 5 章は、本研究の結果をまとめた総括である。

以上要するに本論文は、$Pt/Ti/SiO_2/Si$ 基板のプレアニーリングで sol-gel 法による(111)配向を有する PZT 薄膜が確実に作製でき、さらに sol-gel 法のシードレーヤーの導入により PLD の PZT 薄膜の結晶配向が制御できることを示しており、材料加工プロセス学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。