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Sol-Gel법으로 제조한 PZT(20/80)/PZT(80/20) 이종층 박막의 유전특성

논 문
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Dielectric Properties of PZT(20/80)/PZT(80/20) Heterolayered Thin Films Prepared by Sol-Gel Technique

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Abstract

본 연구에서는 PZT(20/80)과 PZT(80/20) 금속 alkoxide용액을 Pt/Ti/SiO_2/Si 기판위에 상호 반복시킨 강유전성 PZT(20/80)/PZT(80/20) 이종층 박막을 제작하였다. 건조와 소결을 한번 행한 PZT 이종층 박막의 평균 두께는 약 80~90 nm이었다. 제작된 모든 PZT 박막은 rosette상이 없는 치밀하고 균질한 미세구조를 나타내었으며, 하부의 PZT층은 열처리시 상부 PZT 박막의 페로브스카이트 형성에 대해 nucleation site로 작용하였다. 유전상수, 피로특성 및 누설전류특성 등은 단일 조성의 PZT(20/80), PZT(80/20) 박막에 비해 우수한 특성을 나타내었다.

Key Words(중요용어): PZT heterolayered thin films, sol-gel method, nucleation site, dielectric constant, fatigue property, leakage current density

1. Introduction

In recent years, ferroelectric (Ba,Sr)TiO_3(BST), Pb(Zr,Ti)O_3(PZT) and (Pb,La)(Zr,Ti)O_3(PLZT) ceramic thin films have been widely studied in view of their promising use as capacitor or gate dielectric materials for ultralarge-scale integration (ULSI) nonvolatile memory devices larger than 64Mb. In the application to nonvolatile memory devices, PZT thin films are very attractive for application to capacitor of dynamic random access memory (DRAM) due to their high dielectric constant and gate materials of ferroelectric RAM (FRAM) due to their reversible large remanent polarization. Various deposition techniques such as chemical vapor deposition (CVD)[1], sputtering[2], laser ablation[3] and sol-gel method[4] could be used for successful synthesis of PZT system films. Among these processing methods, sol-gel method is especially useful in processing cost reduction, stoichiometric composition control, and large area fabrication. The influence of buffer layer[5] and the effect of electrode materials[6] in PZT films were studied for application to memory devices. Also it is very attractive to stack multiple coatings of different kinds of perovskite dielectric thin films. But only a few works on electrical properties of $PbTiO_3/PbZrO_3$[7], $Pb(Zr,Ti)O_3/(Pb,La)TiO_3$[8] and $BaTiO_3/BaPbO_3$[9] have been undertaken. And there are still few reports on the preparation and dielectric properties of PZT heterolayered films formed by PZT layers of different compositions. The electrical properties of the resultant films prepared by sol-gel process depend on the microstructures of the films including a porosity, orientation of the crystalline phase, interface structure between an electrode and a film.

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In this study, PZT(20/80)/PZT(80/20) hetero-layered thin films were prepared by sol-gel method, which were spin-coated on the Pt/Ti/SiO_2/Si substrate alternately using PZT(20/80) and PZT(80/20) metal alkoxide solutions. It is very easy, by means of sol-gel method, to stack different kinds of thin films by mutiple coating. We investigated the effects of the lower PZT layers on the structural and electrical properties of PZT heterolayered film. And the dielectric properties were also investigated for DRAM applications.

2. Experimental

$Pb(Zr_xTi_{1-x})O_3$ (x=0.20, 0.80) precusor solutions with excess Pb-acetate 10mol% were prepared by Sol-Gel method from Pb-acetate trihydrate [$Pb(CH_3CO_2)_2 \cdot 3H_2O$], Zr n-propoxide[$Zr(OCH_2CH_2CH_3)_4$] and Ti iso-propoxide{$Ti[OCH(CH_3)_2]_4$} as starting materials, and 2-methoxyethanol ($CH_3OCH_2CH_2OH$) as solvent. $Pb(Zr_xTi_{1-x})O_3$ alkoxide solutions were spin-coated on the Pt(150nm)/Ti(100nm)/SiO_2(100nm)/p-Si(100) sub-strates using spinner operated at 4000rpm for 30sec to form the first layer. These $Pb(Zr_xTi_{1-x})O_3$ films were dried at 300℃ for 30min to remove the organic materials, and sintered at 650℃ for 1hr to crystallize them into perovskite structure. And then $Pb(Zr_{1-x}Ti_x)O_3$ alkoxide solutions were spin-coated and dried/sintered on $Pb(Zr_xTi_{1-x})O_3$ films to form the second layer in the same conditions. This procedure was repeated several times, and PZT-n(n: number of coatings) heterolayered thin films were fabricated.

The crystallinity of PZT heterolayered thin films was analyzed by X-ray diffraction(XRD), surface morphologies of the films were examined by scanning electron microscopy(SEM). For electrical measurements, Pt was deposited on the films as top electrodes with a diameter of 250μm. Leakage current density, fatigue and polarization reversal properties were measured.

3. Results and Discussion

Figure 1 show the XRD patterns of the five coated PZT heterolayered film with the lower layer of rhombohedral PZT(80/20) film and tetragonal PZT(20/80) film. In the Fig. 1(a), an intense peak at 2θ=28.5° was observed, which should be identified as pyrochlore phase, often appears in Zr-rich PZT films. On the other hand, Fig. 1(b) shows typical XRD patterns of PZT polycrystalline structure without preferred orientation and no pyrochlore phase is observed.

In general, the activation energy for nucleation of perovskite PZT decreases with increasing Ti content.[10] Therefore, the crystalline phase of PZT

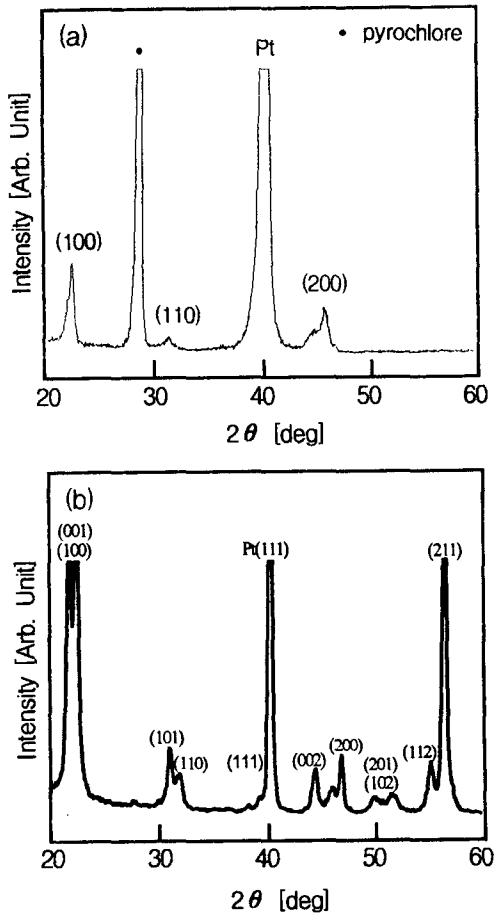

Fig. 1. X-ray diffraction pattern of the five coated PZT heterolayered films with the lower layer of (a) PZT(80/20) film and (b) PZT(20/80).

heterolayered films depend strongly on the composition ratio of Zr/Ti on the lower layer. And it can be assumed that the initial Ti-rich PZT layer plays the important role of dense nuclei and easy crystallization in the succeeding growth of PZT.

PZT heterolayered film with the lower layer of PZT(80/20) and PZT-1, 2 films with the lower layer of PZT(20/80) showed worse electrical properties because of a rich amount of pyrochlore phase and the serial connection with the interfacial layer, like pyrochlore phase between the PZT films and Pt electrode. Therefore the dielectric properties were measured for films with the lower layer of PZT(20/80) coated more than three times.

Figure 2 shows the dielectric constant and the dielectric loss of PZT heterolayered films as a function of frequency. In all films, dielectric constant decreased and dielectric loss increased with increase in the applied frequency. The dielectric constant increases with increase in the number of coatings, and PZT-6 film shows the highest value, 1385 at 1kHz. PZT heterolayered films have high dielectric constant compared with single composition PZT(20/80) film and PZT(80/20) film[11] due to the formation of dense and homogeneous perovskite phase without the presence of rosette-type microstructure. The dielectric loss properties were independent of the number of coatings and below 3.5% at 1kHz in all films.

Figure 3 shows the C-V characteristics of PZT heterolayered films with the applied voltage range from +5V to -5V. Switching voltages were decreased from +3.2V to +2.2V with increased in the number of coatings due to the diminishing of stress induced from the PZT film/electrodes interfaces. The switching voltages with applied the negative voltage is higher than that with the positive bias voltage. It is suggested that the different internal bias voltage at the interface between the upper and lower electrodes and the PZT film were induced by the difference of thermal history of the upper and lower electrodes.

Figure 4 shows the fatigue characteristics of

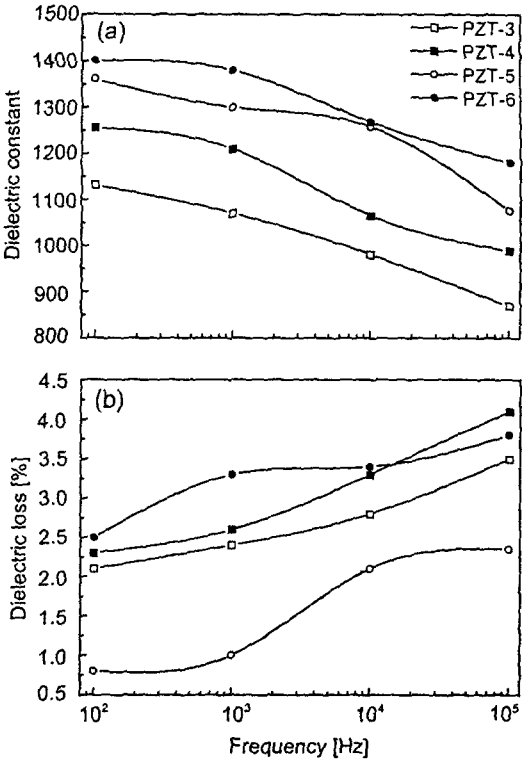

Fig. 2. (a) Dielectric constant and (b) dielectric loss of PZT heterolayered films as a function of frequency.

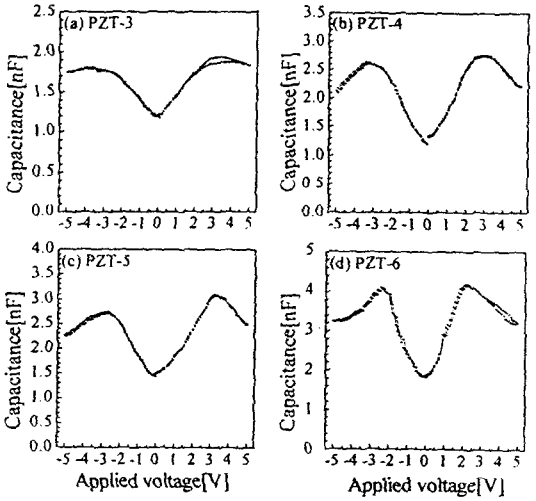

Fig. 3. C-V characteristics of PZT heterolayered films.

PZT heterolayered films, in which remanent polarization and a coercive field are shown as a function of polarization switching cycles. Charge defects, such as Pb vacancy and oxygen vacancy, which are produced as a result of repeated switching, have been considered to be the fatigue origin. These defects can be trapped at electrode-film interfaces, film-film interfaces and grain boundaries because of their low potential energies at the positions.[12] This entrapment of defects results in the loss of polarization. The coercive field increased with the increase of the polarization switching cycles, suggesting that the internal stress was induced by the application of bias voltages.

Figure 5 shows the polarization switching current curves of PZT heterolayered films with the applied voltage. The values of polarization switching time decreased with the increase of the number of coatings and applied voltage. PZT-6 film shows the good switching time of 0.15μsec at $\pm$10V. This phenomenon can be explained by the fact that PZT heterolayered films show a fine and void free grain structure without the presence of pyrochlore phase and rosette type microstructure. And polarization switching time is, generally, in inverse proportion to the applied voltage.

Figure 6 shows the leakage current densities of PZT heterolayered films with applied voltages. Leakage current densities were decreased with the increase in the number of coatings, and these

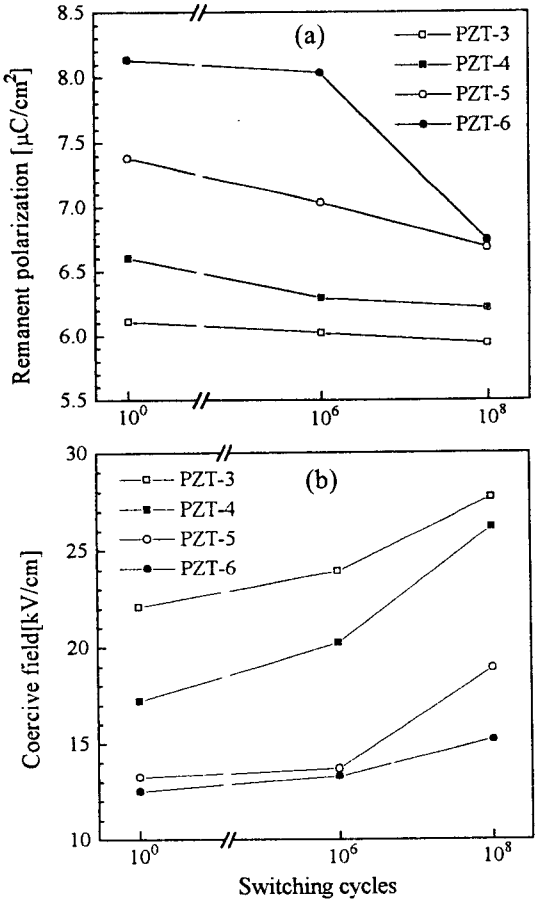

Fig. 4. Fatigue characteristics of (a) a remanent polarization and (b) a coercive field for PZT heterolayered films as a function of switching cycles.

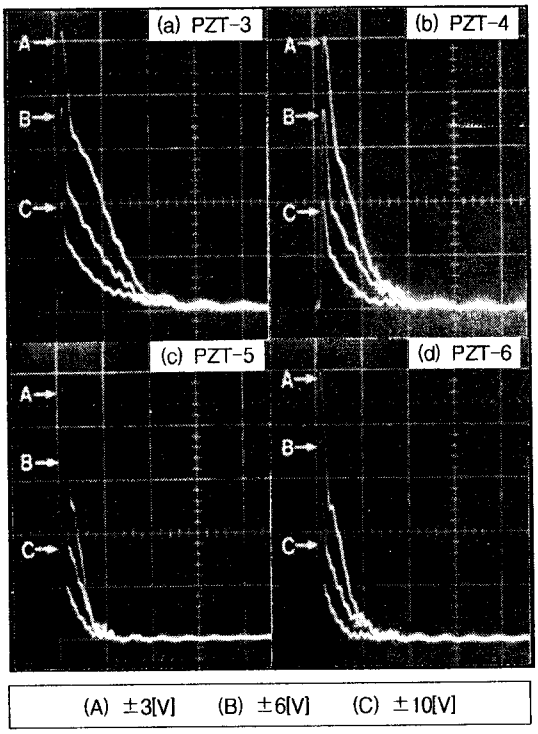

Fig. 5. Polarization switching current curves of PZT heterolayered films with the applied voltage.

were much lower values than those of single composition PZT(20/80) film and PZT(80/20) film. These results suggested that the trap centers of carriers were formed at the interfaces between PZT films, and were increased with an increase of the number of coatings. The leakage current density of the PZT-6 film at 5V was 8.8×10^{-13} A/cm^2. However, further investigations and discussions are necessary to understand the leakage current mechanism in PZT heterolayered films.

Figure 7 shows the resistivity of PZT heterolayered films with the number of coatings. Resistivity was increased with the number of coatings. It is suggested that the trap centers of carriers were formed at the interfaces between the PZT(20/80) films and the PZT(80/20) films, and were increased as the number of coatings increased.[13]

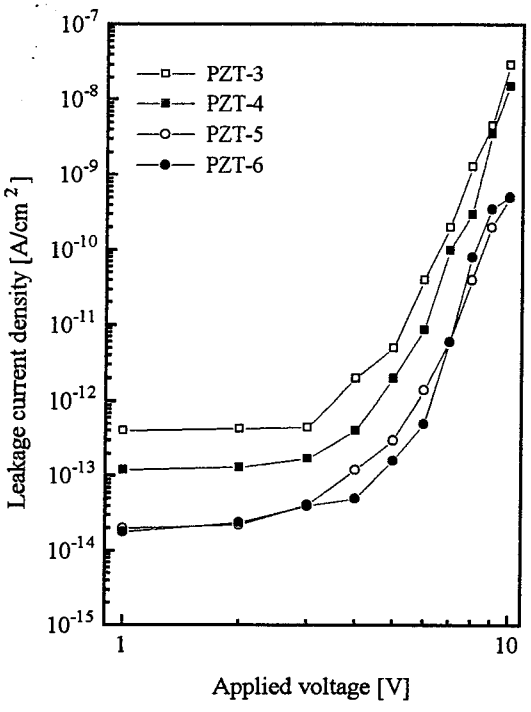

Fig. 6. Leakage current densities characteristics with an applied voltage for PZT heterolayered films.

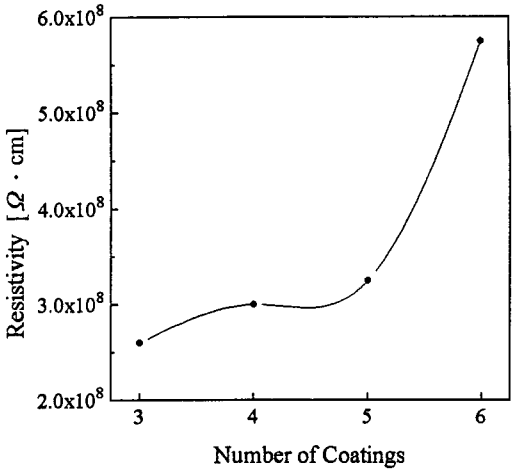

Fig. 7. Resistivity of PZT heterolayered films with the number of coatings.

4. Conclusions

In this paper, PZT(20/80)/PZT(80/20) heterolayered thin films were fabricated by the spin-coating method on Pt/Ti/SiO_2/Si substrates. PZT heterolayered films with the lower layer of tetragonal PZT(20/80) film show dense and homogeneous structure without the presence of rosette-type microstructure. We think that the lower PZT layers provide the nucleation site for the formation of perovskite phase in the upper PZT films. Dielectric properties such as dielectric constant and leakage current densities were superior to those of single composition PZT films, and these values for the PZT-6 film were 1385 and 8.8×10^{-13}A/cm^2 at 5V, respectively. The polarization switching time at ±10V applied voltage and resistivity of the PZT-6 heterolayered films were 0.15 μsec and $5.8\times10^8\Omega$-cm, respectively.

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