CSD-DERIVED FERROELECTRIC THIN FILMS MOLECULAR DESIGN FOR PROPERTIES

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Key words: Chemical solution deposition (CSD), lanthanum nickel oxide, Si wafer

Abstract: Chemical solution deposition (CSD) is the smart and cost effective processing method for advanced materials and thin films. For the smart chemical processing of thin films and nanoparticles by the CSD, molecular design of the precursor is essential. In this study, the importance of the molecular design for the chemical processing is focused on the orientation and residual stress control of the ferroelectric thin films. For the orientaiotn and residual stress control of the ferroelectric thin films, we designed the molecular structure of the ferroelectric thin films and, in some cases, oxide thin film electrode such as lanthanum nickel oxide, $LaNiO_3$ (LNO), which acted as a seeding layer for the orientation control. Namely, we used large side chain groups for the LNO precursor solution to control the film orientation and the residual stress of the ferroelectric thin films, by introducing the nanopores in the LNO layer on a Si wafer to relax the tensile constraint force from a Si wafer.

The other method to relax the tensile stress from a Si substrate with very low coefficient of thermal expansion (C.T.E.) was to reduce the thickness of the Si wafer. The residual compressive stress or strain for the ferroelectric thin film will lead to the following effects; (1) Curie temperature shift towards the higher temperature, (2) Morphotropic phase boundary shift in the case of $Pb(Zr_X Ti_{1-X})O_3$ (PZT), and (3) Enhanced electrical properties. In this study, these effects were experimentally elucidated for the CSD-derived PZT thin films with a composition near MPB.

Feroelektrične tanke plasti izdelane z metodo kemijskega nanosa iz raztopine, CSD – načrtovanje lastnosti s pomočjo molekularne strukture

Kjučne besede: Priprava tankih plasti s sintezo iz raztopin (CSD), Oksidni prevodnik lantanovnikelat (LNO), silicijeva rezina

Izvleček: Priprava tankih plasti s sintezo iz raztopin (Chemicalsolutiondeposition, CSD) je pametna in cenovno ugodna metoda sinteze naprednih materialov in tankih plasti. Za sintezo tankih plasti in nano-delcev je ključno načrtovanje prekurzorjev na molekularnem nivoju. V tem delu je poudarek na pomenu načrtovanja prekurzorjev na molekularnem nivoju za izbrano kristalografsko usmerjenost in kontroliranje napetosti v feroelektričnih tankih plasteh. Načrtovali smo strukturo prekurzorjev feroelektričnih tankih plasti in prevodnih oksidnih plasti na molekularnem nivoju. Oksidni prevodnik lantanovnikelat (LNO) je služil tudi kot nukleacijska plast in omogočil kontrolo kristalografske usmerjenosti feroelektrične plasti. Pripravili smo prekurzor LNO z velikimi stranskimi verigami, iz katerega smo pripravili plasti LNO z nanoporami na silicijevi rezini, na katere smo nadalje nanesli feroelektrične plasti, kar nam je omogočilo kontrolo kristalografske usmerjenosti in napetosti feroelektričnih plasti.

Naslednja metoda relaksiranja nateznih napetosti plasti na podlagah silicija, za katerega je značilen nizek linearni temperaturni razteznostni koeficient, je zmanjševanje debeline podlage. Posledice tega so: (1) pomik Curiejeve temperature k višjim vrednostim, (2) premik morfotropne fazne meje v primeru $Pb(Zr_X Ti_{1-X})O_3$ (PZT) in (3) izboljšane električne lastnosti. V študiji smo omenjene vplive eksperimentalno pojasnili pri tankih plasteh PZTs sestavo blizu morfotropne fazne meje.

1. Introduction

Lead zirconate titanate ($Pb(Zr,Ti)O_3$:PZT) thin films exhibit high potential for ferroelectric random access memories, microactuators and infrared sensors as well as for Micro-Electro-Mechanical Systems (MEMS) because of their excellent ferroelectric, piezoelectric and pyroelectric properties /1/. In order to deposit PZT films, various techniques have been used, such as CSD, sputtering, and metal organic chemical vapor deposition (MOCVD). Among these techniques, CSD has advantages for producing PZT thin film devices due to its simplicity, easy control of homogeneous compositions and film thickness for large substrates, and low processing temperature, as compared with other techniques /2, 3/.

Electrical properties of PZT films are strongly dependent on several factors such as composition, crystal orientation, thin film electrode, and residual stress. Therefore, it is very important to control these factors. For the case of film orientation, (001)-oriented tetragonal PZT films and (111)-oriented rhombohedral PZT films are expected to show good electrical properties. There are many reports on the orientaion control of PZT films /4, 5, 6/. Epitaxial PZT films with different orientations have been deposited on single crystal substrates of MgO and $SrTiO_3$ /7, 8/. However, highly c-axis oriented PZT films deposited on a silicon substrate are required for many advanced devices. It has been reported that a tetragonal PZT should have large Pr value and large d_{33} along /001/ direction even for the rhombohedral PZT after the theoretical calculation /9/. Therefore, it is very important to prepare the (001)-oriented PZT films on a silicon substrate.

There are three strategies to control the PZT film orientation. One is the use of the in-situ seeding layer of good

lattice matching with the PZT. In the previous study, we investigated the effect of the pre-annealing temperature on the orientation of the resultant PZT thin films, in which in-situ seeding layer was formed during pre-annealing /10/. In addition, the novel method of Electric-Field-Assisted Annealing (EFA-A) was demonstrated as the second effective method to control the orientation of the PZT thin films on $Pt/Ti/SiO_2/Si$ substrates through CSD /11/. EFA-A is the method of applying an electric field to thin film during annealing. The XRD intensities of the (001)&(100) planes in the films deposited with an EFA-A increased and that of the (111) plane decreased. However, the ferroelectricity did not improve effectively because the residual cracks still existed in the surface of the films. In this paper, an EFA-A was applied only to the first PZT seeding layer with a same composition. The PZT film was deposited on the seeding layer by rapid thermal annealing (RTA) without an electric field to investigate the relation between crystal orientation, microstructures and electrical properties of the resultant films.

The other factors that affect the electrical properties of the CSD-derived PZT thin films are composition, thin film electrode and the residual stress in the resultant films which strongly depends on the substrate including thin film electrode and the annealing processes as well as the film thickness. The film composition is easy to control if the molecular-designed precursor solution is used. In this paper, we mainly prepared PZT precursor solution with a composition near morphotropic phase boundary (MPB; Pb:Zr:Ti = 120:53:47) and used $Pt/Ti/SiO_2/Si$ substrate because of the compatibility with the semiconductor. Therefore, the last important factor we focused in this paper is the residual stress in the films because ferroelectricity and piezoelectricity should be strongly affected by the residual stress in the films which is strongly affected by the thin film processing.

2. Experimental Procedure

Lead acetate trihydrate, titanium iso-propoxide and zirconium n-propoxide were used as starting materials, and absolute ethanol was used as a solvent to prepare the precursor solution for CSD. The Zr/Ti ratio was mainly 53/47, and excess Pb (20 mol%) was added to the precursor solution to compensate for the lead depletion of lead during processing by the evaporation and diffusion into the platinum electrode. Therefore, the nominal composition of the precursor solution was equivalent to that of $Pb_{1.2}(Zr_{0.53}Ti_{0.47})O_3$. Details of the precursor solution preparation are described elsewhere /12/. The concentration of the PZT precursor solution was controlled at 0.6 M.

Orientation control of the PZT films were carried out by using in-situ seeding layers of (001)-oriented PbO or (111)-oriented Pt/Pb alloy, which could be deposited during pre-annealing at 350 °C or 420 °C. We also used EFA-A to increase the (001)-oriented grains in the films /11/. Final annealing was performed at 650 °C for 5 min. in air by the rapid thermal annealing (RAT).

Crystalline phases in the resultant PZT thin films were identified by X-ray diffraction (XRD). For electrical measurement, Au top electrode was sputtered through the metal mask with 200 or 50μm circular holes. To control the residual stress in the films, we used the back-etching technique to prepare the diaphragm structure with different residual Si substrate thickness /13/.

Dielectric behavior of the resultant PZT thin films was measured by LCR meter (HP-4284A). P-E hysteresis loops and the piezoelectric property for the resultant thin film capacitors were measured by the ferroelectric thin film test system combined with scanning probe microscope (Toyo corporation, FCE-PZ and SII Nanotechnology Inc., SPI3800N).

3. Results and Discussion

3.1. Deposition of highly oriented PZT Film

For the deposition of high performance PZT thin films on a Si wafer, molecular-designed precursor solution is essential. Figure 1 shows the bulk gel of PZT prepared by the careful aging of the precursor solution in a humidity to proceed partial hydrolysis and following polycondensation for a very long period.

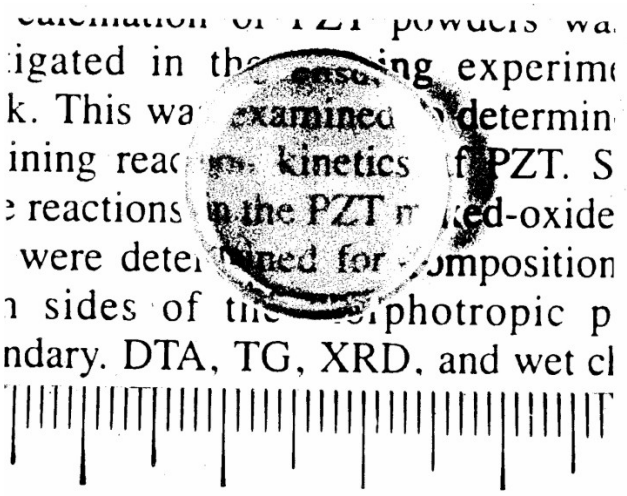

Fig.1 Bulk PZT gel from molecular-designed precursor solution prepared by the aging in a controlled humidity. (after one year aging)

As shown in Fig.1, large and transparent PZT gel was obtained after the long aging, showing the very high homogeneity of the precursor solution, in which metal-oxygen-metal bonding was successfully formed. From such precursor solution, we can easily deposit highly oriented PZT thin films even on the semiconductor compatible $Pt(111)/Ti/SiO_2/Si$ substrate if the proper annealing process was selected. We chose the RTA for the deposition of highly oriented PZT thin films with a MPB composition by using in-situ seeding layers and EFA-A treated PZT seeding layer.

Figure 2 shows the lattice matching of the seeding layers used in this study. By using these seeding layers, we successfully deposited the highly (111)- and (001)&(100)-oriented PZT thin films with different compositions on a Pt(111)/Ti/SiO_2/Si substrate. Figures 3 and 4 exhibit the XRD patterns and cross-sectional images of scanning electron microscope for the PZT films with tetragonal and rhombohedral symmetries.

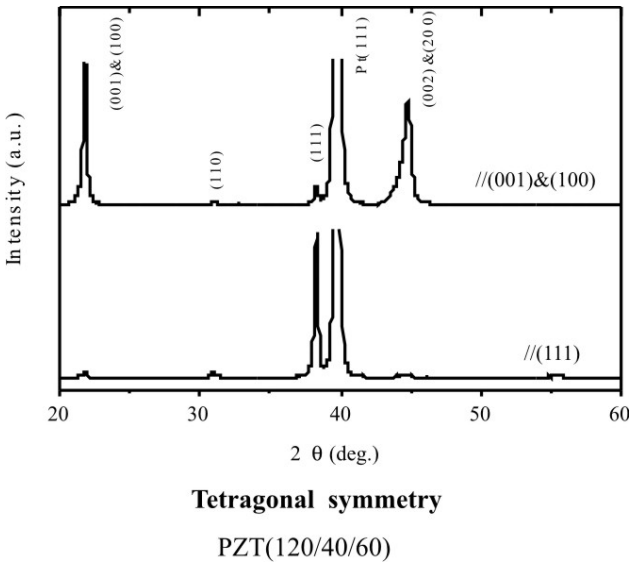

Fig.3 a XRD patterns for PZT thin films with tetragonal symmetry.

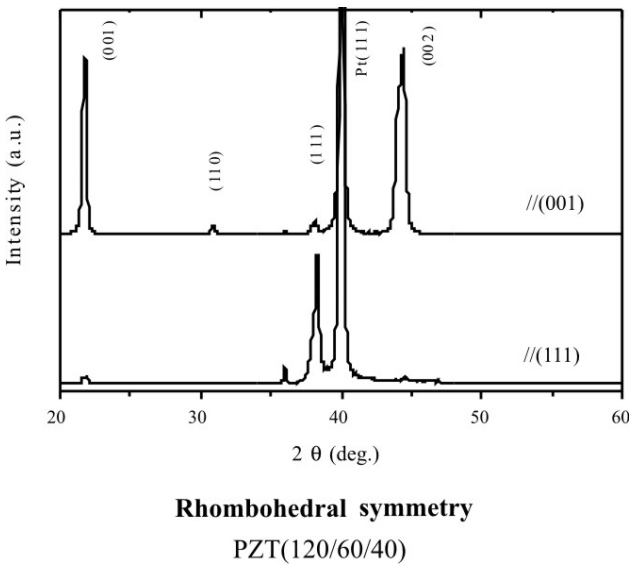

Fig.3 b XRD patterns for PZT thin films with rhombohedral symmetry.

XRD results demonstrated that highly oriented PZT thin films more than 90% degree of orientation could be deposit by using the in-situ seeding layers for both directions in wide compositional region.

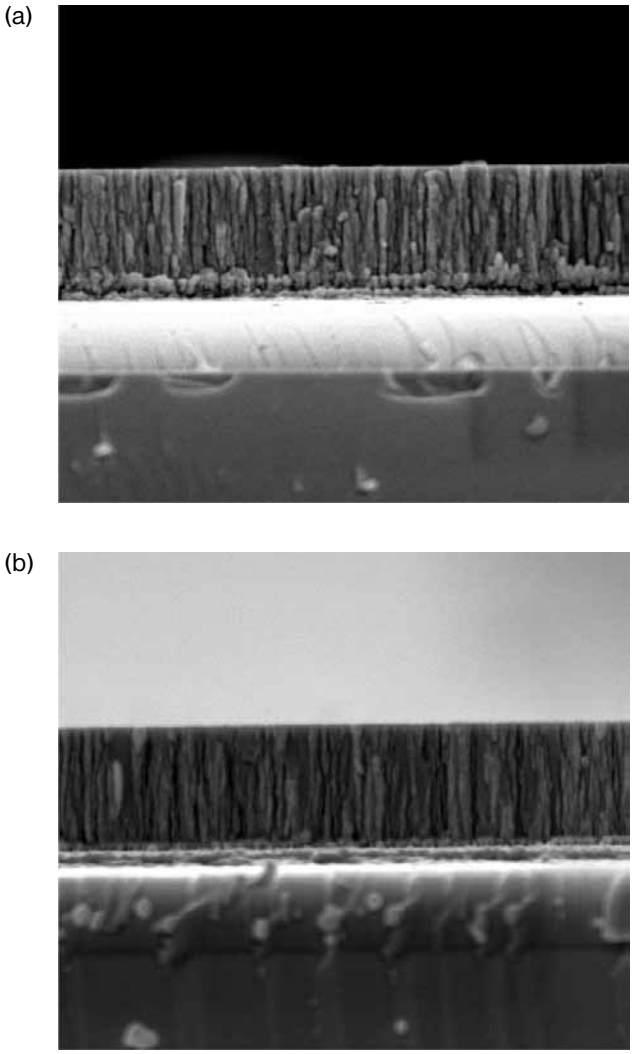

Fig.4 Cross-sectional SEM images for CSD- derived PZT thin films of MPB composition with (a) (111)- and (b) (001)&(100)- orientation.

In addition, all these films exhibited nice columnar structure of relatively large grain size. Therefore, we can expect good electrical properties for these films, especially for the PZT films with a MPB composition. Orientation mechanism was described elsewhere /14/

3.2. Electrical properties of highly oriented PZT thin films

Molecular design of the precursor solution and the use of seeding layer allowed to deposit highly oriented PZT thin films on a Pt(111)/Ti/SiO_2/Si substrate, especially for the case of the (001)&(100)-oriented films which was expected to exhibit good electrical properties. Therefore, we measured the electrical properties of these oriented PZT thin films. Figure 5 shows effective d_{33} values for the highly oriented PZT thin films. The effective d_{33} values were measured by the continuous charge integration (CCI) method /15/. The effective d_{33} value measured by CCI method includes not only true d_{33} value but also d_{31} and d_{15} values because of the bending effect. Therefore,

the effective d_{33} values measured by CCI method are relatively larger than those measured by SPM method with small top electrode. However, CCI method is useful to compare the effective d_{33} values for thin films because of its simplicity. Those two method exhibited same tendency for the piezoelectricity of the PZT thin films as shown below in this paper.

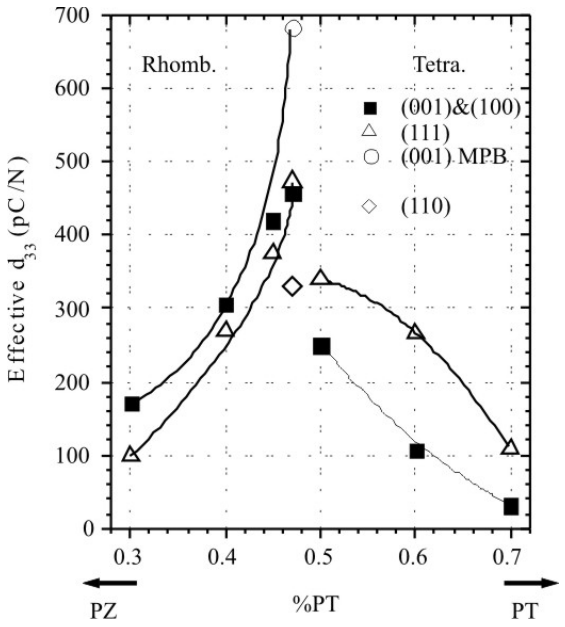

Fig.5 Relation between effective d33 and the compositions for PZT thin films with different film orientations.

Figure 5 demonstrated that CSD-derived highly oriented PZT thin films exhibited highest and excellent piezoelectricity at a MPB composition. In addition, (001)&(100)-oriented films exhibited higher effective d_{33} values in the case of the rhombohedral symmetry, according to the theoretical calculation /9/. On the other hand, (111)-oriented PZT thin films exhibited higher effective d_{33} value than the (001)&(100)-oriented films. This behavior is controversial collision with a theoretical calculation. We postulated that this behavior was ascribed to the domain orientation in tha (001)&(100)-oriented PZT thin films in the tetragonal region. Then, we tried to deposit highly (001)-oriented PZT thin films in a tetragonal region by using EFA-A derived PZT seeding layer together with a PbO seeding layer. As a result, we successfully deposited highly (001)-oriented PZT thin films with degree of orientation more than 95 % by the XRD measurement. Figures 6 and 7 show the dielectric constant and effective d_{33} values for the PZT thin films with different composition and film orientation. Because the single crystals of PZT with a MPB composition have not been prepared, we can not compare the actual values of dielectric and piezoelectric constants for the highly oriented PZT thin film and single crystal near the MPB composition. However, these values have been calculated /9/.

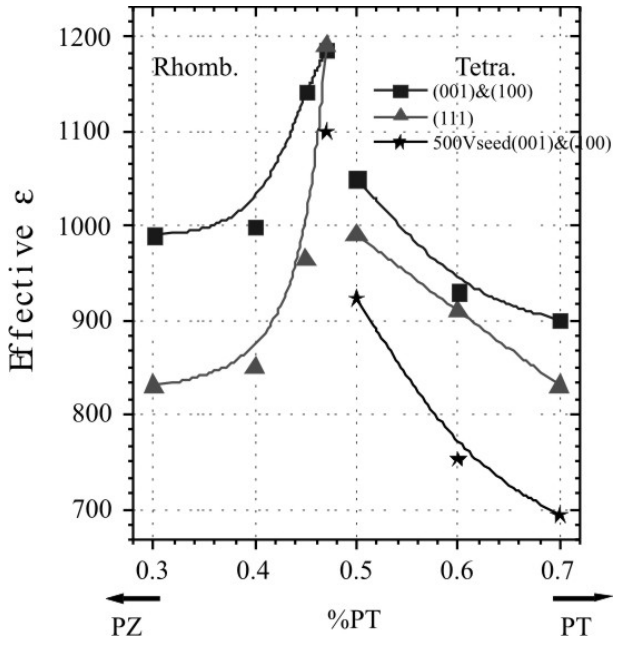

Fig.6 Relation between dielectric constant and composition of PZT thin films with different orientations.

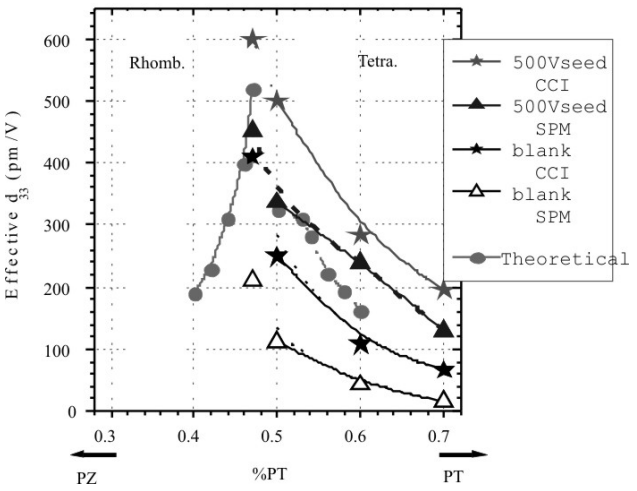

Fig.7 Relation between effective d_{33} and composition of PZT thin films with different orientations.

For the case of dielectric constant, highly (001)-oriented PZT films deposited on the EFA-A derived seeding layer exhibited lower dielectric constants in the tetragonal region according to the theoretical calculation. This is ascribed to the increase in the (001)-oriented grains in the PZT thin films with a tetragonal symmetry, which means the dielectric constant along the a-axis is higher than that along the c-axis in the tetragonal region of PZT. Then, we compared the effective d_{33} values for the PZT thin films in the tetragonal region by using the CCI method and SPM method, as shown in Fig.7. Figure 7 clearly showed the higher effective d_{33} for the films deposited by the EFA-A in the tetragonal region and exhibited still very high effective d_{33} value more than 400 (pm/V) even if measured by the SPM method.

This value is the highest one for the PZT thin film with a MPB composition measured by the SPM method. Therefore, this figure demonstrated that highly c-axis oriented PZT thin films should exhibit higher piezoelectricity independent of the composition, showing the good agreement with the theoretical calculation after Du et al. /9/.

3.3 Stress induced gigantic piezoelectricity

For the better electrical properties of the CSD-derived highly oriented PZT thin films, residual stress in the resultant films should be controlled. In addition, residual stress could be changed by the device structures. Therefore, we chose the diaphragm structure as the actual device structure which could be used for the MEMS devices. Previous study have reported that the residual stress in the lead titanate thin films on the diaphragm structure with different residual thickness of Si substrate dramatically increased up to around 1.6 GPa, if the residual thickness of Si substrate was decreased below 150mm as shown in Fig.8. Therefore in this study, highly oriented PZT thin film with a MPB composition was deposited on the diaphragm structure with different residual thickness of Si substrate and the piezoelectric constant for the PZT thin films were measured by the SPM method to elucidate the effect of the residual stress in the film. Figure 9 shows the effective d_{33} values for the PZT thin films with a MPB composition on a diaphragm structure with different residual thickness of Si substrate. As a result, effective d_{33} values dramatically increased at the residual thickness of the Si substrate was 50 μm and reached more than 400 (pm/V). For the case of the lead titanate thin films on the same substrate structure, the residual stress in the films dramatically increased if the residual thickness of Si substrate was decreased below 150μm and reached platoe at aroud 50μm. Therefore, the higher effective d_{33} value for the PZT thin film on the diaphragm structure with 50μm residual thickness of Si substrate could be ascribed to the residual compressive stress in the film, showing the stress induced gigantic piezoelectricity. This value is almost same as that of the PZT thin film deposited by using both PbO and EFA-A derived PZT seeding layers. However, in this case, we did not use the EFA-A derived PZT seeding layer. This indicated that the residual stress in the film played an important roll for the piezoelectricity of the resultant PZT thin film.

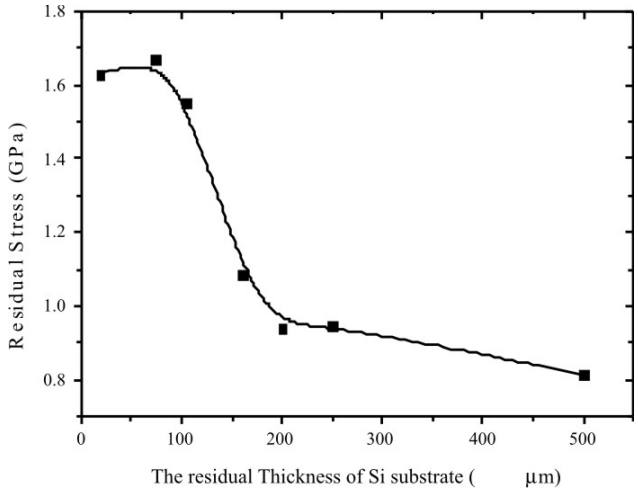

Fig. 8 Relation between residual stress in films and residual thickness of Si substrate measured by raman spectroscopy[13].

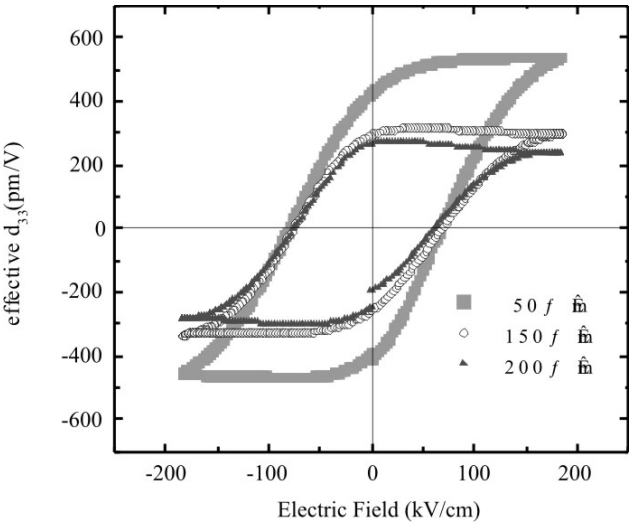

Fig.9 Effective d_{33} for PZT thin films with a MPB composition and different residual thickness of Si substrate.

4. Conclusions

This paper focused on the total processing of the CSD-derived PZT thin films on the Pt/Ti/SiO_2/Si substrate, including the orientation control method and the stress induced gigantic piezoelectricity. For the highly oriented PZT thin films on a semiconductor compatible Pt/Ti/SiO_2/Si substrate, molecular-designed precursor solution and the suitable seeding layers were essential. The electrical properties of the resultant thin films with different orientations were elucidated by using several methods. These measurements demonstrated that highly oriented PZT thin films exhibited reasonable electrical properties and showed good agreement with those of the theoretical values. In addition, piezoelectric measurement for the highly oriented PZT thin films on the diaphragm structure exhibited the importance of the residual stress in the film. This paper demonstrates that residual stress control is another essential factor for the high performance MEMS devices, even for the highly oriented PZT thin films.

5. Acknowledgements

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6. References

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