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Preparation and electrical properties of thick PZT films deposited on alumina substrates with Ag-Pd electrodes and Pt plates by spin-on process

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Ag-Pd/알루미나 및 Pt전극에 스핀온 방법으로 제조된 PZT후막의 전기적 특성

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Abstract The electrical properties of thick PZT films deposited on Ag-Pd/Al_2O_3 and Pt electrodes were carefully investigated according to the annealing methods and the substrates. For electrical properties measurements, silver was deposited on PZT films as top electrode. The crystallogaphic structure of the films was examined by standard X-ray diffraction method to determine which crystalline phase was present. Dielctric constant was measured at 1 kHz, 10 mV by using a HP4284A. The electrical properties of PZT films with 3 wt% PbO addition were not improved. It was also found that the Ag-Pd layer has a good possibility as electrode instead of Pt. It seems clear from the present experiments that the thick PZT films having the good electrical properties can certainly be obtained using spin on technique combined with rapid thermal annealing.

요 약 Ag-Pd/Al_2O_3 와 Pt 기판에 스핀온 방법으로 제조된 PZT 후막의 열처리 방법에 따른 전기적 특성을 조사하였다. 전기적 특성을 측정하기 위하여 상부전극으로 은(Ag)을 PZT표면에 증착하였다. 이렇게 만들어진 PZT 후막의 결정구조는 X-ray로 조사하였으며, 유전상수는

HP4284A를 사용하여 1 kHz, 10 mV에서 측정하였다. 또한 유전계수는 Berlincourt 피에조메터를 사용하여 측정하였다. 그 결과 3 wt% PbO가 첨가된 PZT 후막의 전기적 특성은 오히려 감소하였으며, Ag-Pd 전극은 Pt 전극을 대체할 수 있는 가능성이 매우 높았다. 특히 스핀온 방법으로 제조된 PZT 후막을 급속열처리(RTA)를 함으로써 전기적 특성을 크게 향상시킬 수 있었다.

1. Inroduction

Ferroelectric films, such as $PbZr_xTi_{1-x}O_3$ (PZT), offer the potential applications for important device including transducers, infrared detectors and memory devices because of their excellent electromechanical properties [1].

It is important and necessary for device application of PZT films to obtain the excellent crystallinity and the expected electrical properties. However, these properties depend on the annealing methods, electrodes and the preparation techniques such as sputtering, chemical vapor deposition (CVD), laser ablation and the sol-gel process [2].

In this study , we prepared the PZT films by the spin-on technique method which has advantage of a low cost and is well suited to the mass production. We also take the new approach to achieve excellent crystallinity and excellent electrical properties of sintered PZT films. The Ag-Pd/Al_2O_3 structure and the bulk Pt were used for bottom electrodes. PZT films prepared by spin-on technique were annealed by both conventional furnace and rapid thermal processes. The effect of the various preparation conditions on the electrical properties of PZT films will be discussed.

2. Experimental

We used a $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT (50/50)) powder with and without 3 wt% PbO dopping as ferroelectric materials. The PZT powders were prepared by a coprecipitation process described in previous papers [3,4]. Thick PZT films with and without 3 wt% PbO addition were deposited on Ag-Pd/Al_2O_3 and Pt substrates by the spin-on after mixing the PZT powder with an organic vehicle to obtain the necessary rheological characteristic. These deposited films were dried at 70℃ for 4h, calcined at 500℃ for 5h, and subsequently annealed at 1050℃ either for 1h or for 30 second in air atmosphere by using the conventional furnace and the rapid thermal annealing (RTA), respectively.

We also prepared samples annealed at 1050℃ by RTA without calcining at 500 ℃ for 5 h The dielectric contant εr and the piezoelectric coefficient d33 were measured by a HP4284A apparatus and a Berlincourt piezometer, respectively after depositing a silver (Ag) on the PZT films as top electrode.

The thickness of PZT films was controlled by laser doppler vibrometry technique. Crystalline structure of the obtained PZT films were analyzed by X-ray diffraction (XRD) with the Cu-Kα emission. The finally capacitor structures are Ag/PZT/Ag-Pd/Al_2O_3 and Ag/PZT/Pt.

3. Results and discussion

The crystallographic structure of the films was examined by standard X-ray diffraction (XRD) method to determine which crystalline phase was present at various annealing conditions. X-ray diffractometer with a Cu anode was used. The structure of the films was analyzed by comparing the XRD patterns with crystallographic information reported earlier on PZT ceramics [5]. X-ray diffraction patterns of the PZT films deposited on the Ag-Pd/Al_2O_3 substrates, which were processed rapid thermal annealing at 1050 ℃ for 30sec. after calcining at 500℃ for 5h, was shown in Fig. 1.

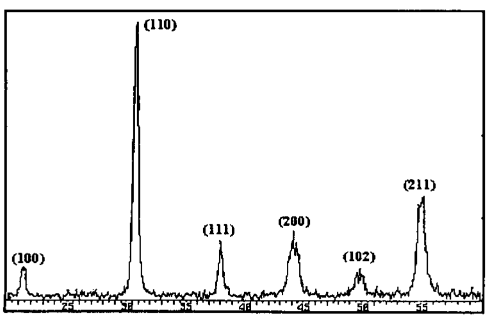

Fig. 1. X-ray diffraction pattern of PZT films deposited on Ag-Pd/Al_2O_3 substrates.

Figure 1 revealed that the samples consist of the perovskite phase without any pyrochlore phase within the detection limit of XRD and have a <110> preferred orientation. The other samples deposited on the Pt substrates have the same X-ray pattern like Fig. 1, even though the other samples were not shown in this paper.

Dielectric constant can be obtained by measuring the cappacitance of Ag/PZT/Ag-Pd/Al_2O_3 capacitor structure like the previous paper [6].

In this study, dielectric constant was measured at 1 KHz, 10 mV by using a HP 4284 A apparatus. Figure 2 shows the thickness dependence on dielectric constants of PZT films deposited on Ag/PZT/Ag-Pd/Al_2O_3 substrates with and without 3 wt% PbO addition. The deposited PZT films were heat treated at 1050℃ for 1h by converntional furnace annealing after calcining at 500℃ for 1 h. Although the grain size does not depend on the thick-

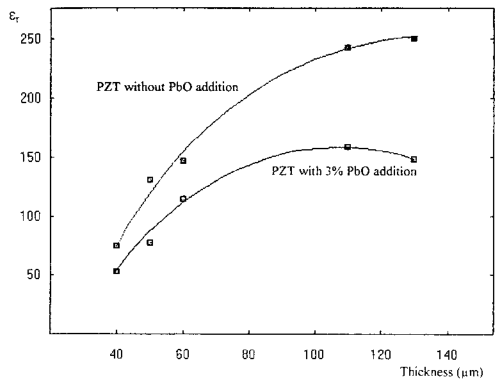

Fig. 2. The thickness dependence on dielectric constants of PZT films with and without 3 wt% PbO addition deposited on Ag-Pd/Al_2O_3 substrates.

ness, the dielectric constant of PZT films with and without 3 % PbO addition have the value range from 74 to 250, 52 to 148 respectively within the measured thickness.

It was found that the samples without 3 wt% PbO addition had a higher dielectric constant than those with 3 wt% PbO addition. It is considered that the 3 wt% PbO addition do not play the roles of improving the dielectric constant. Dielectric tangent loss of both samples were also ranged from 1.5 to 0.4 %.

Figure 3 shows the change of dielectric constant for PZT films deposited on Ag-Pd/Al_2O_3 and Pt substrates versus the measured film thickness. Both samples were same heat treated like the Fig. 2. As can be seen, the dielectric constant of PZT films deposited on the Ag-Pd/Al_2O_3 substrates was clearly increased with the

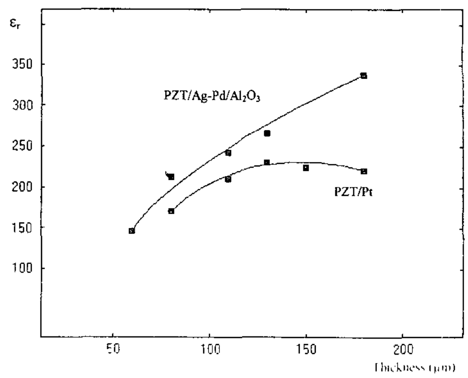

Fig. 3. The change of dielectric constant for PZT films deposited on Ag-Pd/Al_2O_3 and Pt substrates versus the measured film thickness.

film thickness and had the higher value than that of Pt substrates within the measured thickness range. In the case of Pt substrates, the dielectric constant was gradually increased and stayed constant above the 130 μm thickness. It is considered that the Ag-Pd layer plays the two roles of improving the adhesion and de-

Table 1
Comparison of dielectric constant and piezoelectric coefficient on the three type samples processed different annealing conditions

	Annealing condition	Substrate	Dielectric constant(ε_T)	Dielectric loss (tan δ, %)	Piezoelectric coefficient(d_{33})
Type A	500℃(5h)+1050℃(1h): conventional furnace annealing	Ag-Pd/Al_2O_3	194	0.5	74
Type B	500℃(5h)+ 1050℃(30sec) : rapid thermal annealing(RTA)	Ag-Pd/Al_2O_3	289	0.7	105
Type C	500℃(20sec)+ 1050℃(30sec) : rapid thermal annealing(RTA)	Ag-Pd/Al_2O_3	310	0.65	

creasing the internal stress of PZT films.

Table 1 shows a comparison of dielectric constant values and piezoelectric coefficient the three samples (type A, type B, type C) without 3 wt% PbO addition processed in different annealing conditions at a 80 μm thickness of PZT film. When the dielectric constant of three type samples are compared, type C sample annealed at 1050℃ for 30 seconds by RTA without calcining at 500℃ for 30seconds by RTA with calcining at 500℃ 5 h which is preferentially oriented in the <110> direction as discussed in previous, shows higher dielectric constant than other samples. The dielectric constant values measured at 1 kHz were 194, 289, 310 for the type A, B and C sample respectively far from the 1000 value of the bulk PZT ceramics. These data show the strong dependence of dielectric constant on the annealing method. However the type C sample is not adapted to the device due to its poor mechanical properties. A similar phenomenon is also observed in the Ag/PZT/Ag-Pd/Si samples which are not shown in this paper. From these results, it was found that the type B sample annealed at 1050℃ for 5 h had the optimal annealing conditions. Further works will be in progress for enhancing the electrical properties by changing the RTA process.

Measurements of the piezoelectric coefficient d33 were carried out on type A and type B sample, directly with a Berliucourt d33 meter, or using a laser interferometer with a lock-in amplifier to measure the field-induced displacements of the film.

The results obtained with these two methods are quite similar and show a significant improvement of this coefficient when using the RTA. For a 80 μm thickness film the values were 70 pC/N for type A and 105 pC/N for type B annealed at 1150℃ respectively, which must be compared with the 240 pC/N value of the PZT bulk ceramic of equivalent composition.

4. Conclusions

In summary; this work describes annealing conditions which realize formation of the <110> oriented PZT films on Ag-Pd/Al_2O_3 and bulk Pt substrates and their electrical properties were carefully compared. Even though the PZT films of type C had a high dielectric constant value, they showed poor mechanical properties which could not be applied to the device. Type B sample showed the good dielectric properties such as dielectric constant and pizoelectic coefficient. The electrical properties was not improved in PZT films with 3 wt% PbO addition. It was also found that the Ag-Pd layer is a good possibility as electrode instead of Pt-layer. It seems clear from the present experiments that the thick PZT films having the good electrical properties can certainly be obtained using spin on technique combined with rapid thermal annealing

(RTA) after calcining at 500℃ for 5 h of Ag-Pd/Al_2O_3 electrodes.

Acknowledgements

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