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Propose of New Mixture Target for Low Temperature and High Rate Deposition of PZT Thin Films by Reactive Sputtering

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1. Introduction

In recent years, there has been increasing interest in ferroelectric thin films, in particular, PZT thin films for use in nonvolatile RAM, DRAM, and so on. To ensure compatibility with the silicon ULSI process, a processing temperature below 500℃ is desirable. In order to realize a low temperature growth process, we have been developing a rf reactive sputtering technique using a new (ZrTi+PbO) target system consisted.[1] we have prepared ferroelectric PZT films using the composite target, and found that the perovskite PZT films could be obtained at a temperature as low as 450℃ with good electrical performance because of no inter-diffusion and 2--3 times higher deposition rate than that from the ceramic target.[2-3] As the target structure is unstable in the composite target, we propose a mixture target for quasi-metallic mode which react metal atoms with oxygen molecules on the substrate.

2. Experimental

PZT thin films were prepared using a conventional (not magnetron) rf diode sputtering apparatus. (Table 1) The composite target, as shown in Fig.1, consisted of PbO pellets 13 mm in diameter and 2 mm in thickness positioned on a 100 mm- diameter ZrTi (50%/50%) alloy plate. The target composition is defined as (ZrTi+xPbO) which x is area ratio of target surface $S_{PbO}/(S_{PbO}+S_{ZrTi})$, where S_{PbO} is the total surface area of PbO pellets and S_{ZrTi} is the uncovered surface area of ZrTi target.

Fig. 2(a) is the cross section of Fig. 1. Fig.2(b) is an imaginary target equivalent to the Fig. 2(a), where the holes with the diameter of PbO pellet are dug through and the PbO pellets are put in. Films prepared using this target should be the same as those using Fig. 2(a). If the imaginary target of Fig.2(b) were smashed, mixed and caked, a mixed target will be completed. It has identical function to Fig. 2(a) or Fig. 2(b). According to the imagination, it is considered feasible to fabricate the mixture target as in Fig. 2(c) using Zr, Ti, and PbO powder. They are pressed into the mixed target.

3. Results and discussions

Since we have been aiming at high rate PZT film preparation in the quasi-metallic mode, we selected O_2/Ar flow rate ratio of 2.1%. The deposition rate is as high as 12 [nm/min] which is comparable to that of magnetron sputtering. The structure of various films prepared is analyzed by XRD method. At 450℃, the films exhibit the pure perovskite PZT phase. The temperature range in which the pure perovskite phase is obtained becomes wider as x increases.

Table 1. PZT thin film sputtering conditions

Target	ZrTi (50%/50%) (Purity : 99.99%) PbO powder (Purity : 99.999%) Zr powder (Purity : 98%) Ti powder (Purity : 98%)
RF input power	200 W
Substrate temperature	190℃ to 600℃
Ar gas pressure	10 mTorr (6.94 sccm)
Sputtering gas	Ar + O2
Substrate	Fused quartz glass Pt/Ti/SiO2/Si
Target-substrate distance	62 mm

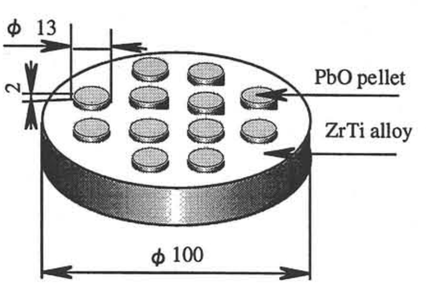

Fig. 1. Schematic diagram of the ZrTi alloy target with PbO pellets.

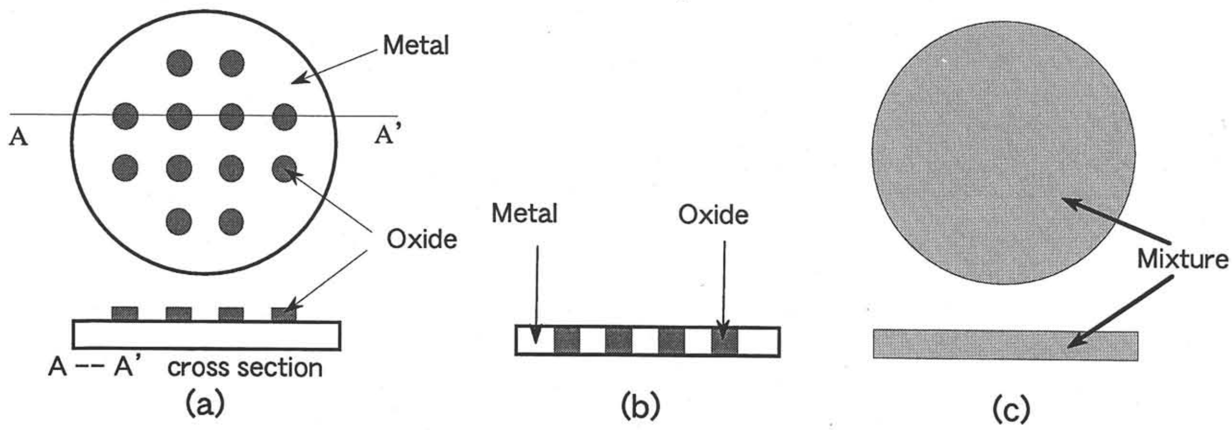

Fig.2 Exolanation Diagram of (a) metal-ceramic composite target, (b) composit target with imaginary hole and (c) mixture target consited of Zr,Ti, and PbO powder.

To examine the interface diffusion of the PZT/Pt/Ti /SiO_2/Si specimen, the depth profile was measured using the SIMS method. For the PZT film prepared at 450℃, as shown in Fig. 3(a), a clear interface between PZT and Pt can be found, and is mainly attributed to the low substrate temperature, while some mixing is observed in the underlying electrode. Inter diffusion between the PZT film and the substrate and mixing are enhanced with increasing growth temperature, as shown in Fig. 3(b) 570 ℃. Thus, the low temperature process is useful.

Because the pure perovskite phase was obtained in the quasi-metallic mode at the growth temperature of 450℃, we selected 450℃ to investigate O_2/Ar flow rate ratio dependence. In the O_2/Ar flow rate ratio range from 2.1% to 4.3%, pure perovskite PZT films are obtained also, which is the similar to that for the composite target. At higher O_2/Ar flow rate ratio, a mixture of PbO, pyrochlore and perovskite PZT phases is obtained. Figure 4(a) shows the XRD pattern of the PZT film prepared in the quasi-metallic mode at O_2/Ar = 2.1% and (b) shows the XRD pattern of the film prepared in the oxide mode at O_2/Ar = 1/1. To examine the electrical properties of the films, Au upper electrodes with 300 μ m diameter were evaporated on the PZT films. Figure 5(a) shows the P-E relationship of the PZT film prepared using the (ZrTi+30%PbO) composite target at 450℃ with the remanent polarization Pr of 20 μ m/cm^2 and the coercive electric field Ec of 150kV/cm, and (b) does the result of the PZT film prepared using the (ZrTi+30%PbO) powder target at 450℃ with the Pr =31 μ m/cm^2 and Ec =130kV/cm, which shows better electrical performance.

4. Conclusions

we proposed the mixture target consisted of Zr, Ti and PbO. To confirm its efficiency, fundamental experiments were carried out using the powder target at 450℃. It was found that at O_2/Ar=2.1% the film that is almost identical to that prepared using the composite target could be obtained. Therefore, the mixture target was proved to be efficient. The method can be applied for various metal oxide and composite film preparation. Moreover, because reaction occurs on the substrate surface, it is considered that this method is effective for laser ablation and reactive evaporation also.

References

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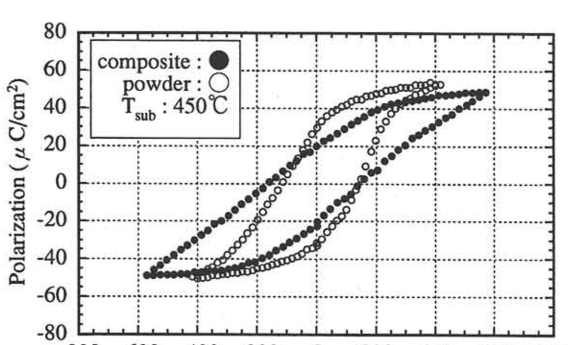

Fig.5 P-E hysteresis characteristics at the growth temperature of 450℃ for (a) the composite target and (b) the powder target.

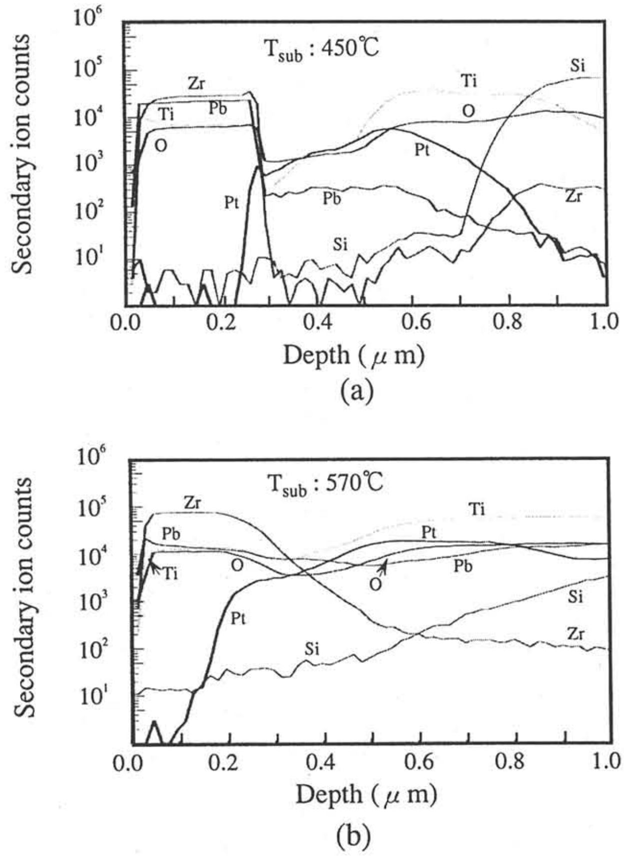

Fig. 3. SIMS depth profiles of the PZT films prepared at (a) 450℃ and (b) 570℃.

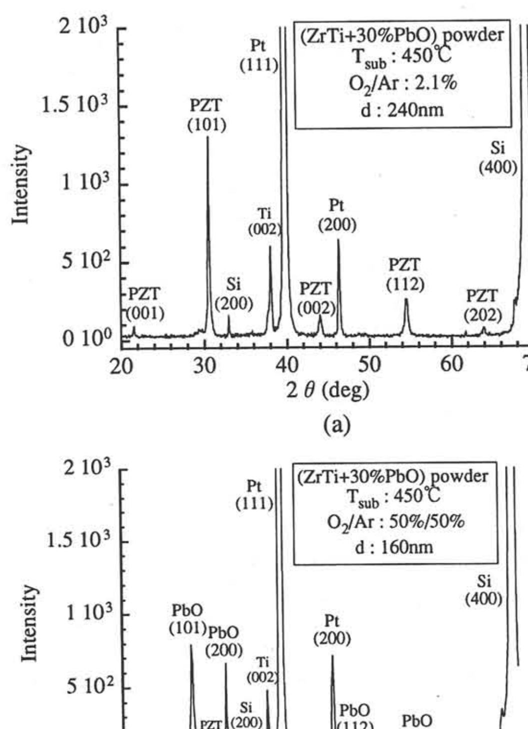

Fig. 4. XRD patterns for the (ZrTi+30%PbO) powder target (a) in quasi-metallic mode (O_2/Ar=2.1%) and (b) in oxide mode (O_2/Ar=1).