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# PROPOSE NEW MIXTURE TARGET FOR LOW-TEMPERATURE AND HIGH-RATE DEPOSITION OF PZT THIN FILMS BY REACTIVE SPUTTERING

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## ABSTRACT

A rf reactive sputter deposition technique was adopted to deposit ferroelectric lead zirconate titanate (PZT) thin films with high rate from a ZrTi alloy target combined with PbO pellets. Deposition characterisitics including the effects of PbO are ratio were discussed. A new deposition mode called the quasi-metallic mode was observed. Perovskite PZT films were prepared at a growth temperature as low as 450℃. However, because the target structure is unstable, weproposed a mixture target consisted of Zr, Ti and PbO. Fundamental experiments were investigated using the powder target. Perovskite PZT film could be obtained at 450℃ with better electrical properties also.

## INTRODUCTION

In recent years, there has been increasing interest in ferroelectric thin films, in particular, PZT thin films for use in nonvolatile random access memories, dynamic random access memories, piezoelectric and pyroelectric devices. Various deposition techniques, such as magnetron sputtering, ion beam sputtering, vacuum evaporation, chemical vapor deposition (CVD), laser ablation, and sol-gel metods are being developed[1-4]. Figure 1 sho-ws the reported growth temperature range in which ferroelectric PZT films were prepared directly on metal electrodes using the above techniques. Temperature higher than 500℃ are necessary to obtain the ferroelectric films in all the techniques. However, to ensure compatibility with the silicon ULSI process and to suppress interdiffusion bet-

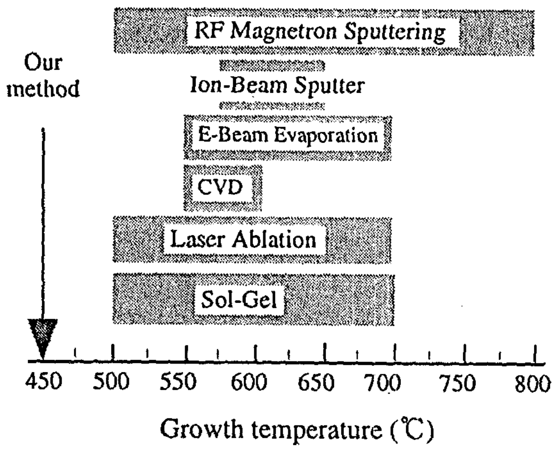


Fig. 1. Substrate temperature dependence of ferroelectric PZT films prepared directly on metal electrodes on growth techniques.

ween the film and the underlying electrode, 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. It is well known that in the reactive sputtering for metal target there are two modes, that is, metallic mode and oxide mode. We speculated that ferroelectric PZT films could be prepared at low substrate temperature, considering that sputtered metal atoms would react with oxygen molecules on the substrate and have larger mobility under the metallic mode condition. Accordingly, we attempted to prepare 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 and 2-3 times higher deposition rate than that from the ceramic target. Moreover, the interdiffusion between the PZT film and the substrate was suppressed by the low growth tenperature.[5, 6]

Therefore, if we pay attention to target structure, the low-temperature and high-rate deposition is possible. However, it is difficult to apply the composite target in practice due to its instability. To solve this problem, we propose a mixture target exactly equivalent to the composite target.

In this paper, using both the composite target and the mixture powder target, we prepared PZT films on $Pt/Ti/SiO_2/Si$ substrates, investigated the fundamental characteristics of te rf reactive sputtering with changing $O_2$/Ar flow rate ratio, and compared the film properties. It is presented that low temperature deposition is possible using both targets with the small difference in the film characteristics.

## EXPERIMENTAL

PZT thin films were prepared using a conventional rf diode sputtering apparatus (non-magnetron). The composite target, as shown in Fig. 2, consisted of PbO pellets 13㎜ in diameter and 2㎜ in thickness positioned on a ZrTi (50%/50%) composite metal plate 100㎜ in diameter. The target composition is defined as (ZrTi+$\chi$PbO) which 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 surfce area of ZrTi target.

The powder target is considered as follow : Figure 3(a) is the cross section of Fig. 2. Figure 3(b) is an imaginary target equivalent to the Fig. 3(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 sme as those using Fig. 3(a). Figure 3(c) is the target in which the PbO pellets and ZrTi plate are

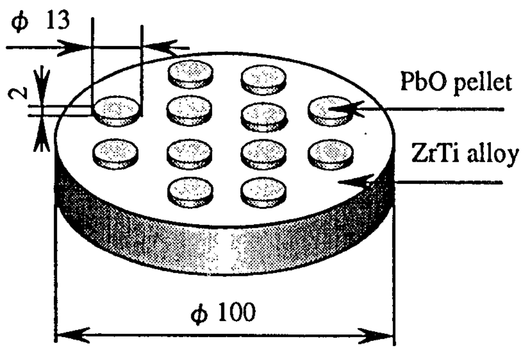


Fig. 2. Schematic diagram of the ZrTi alloy target with PbO pellets.

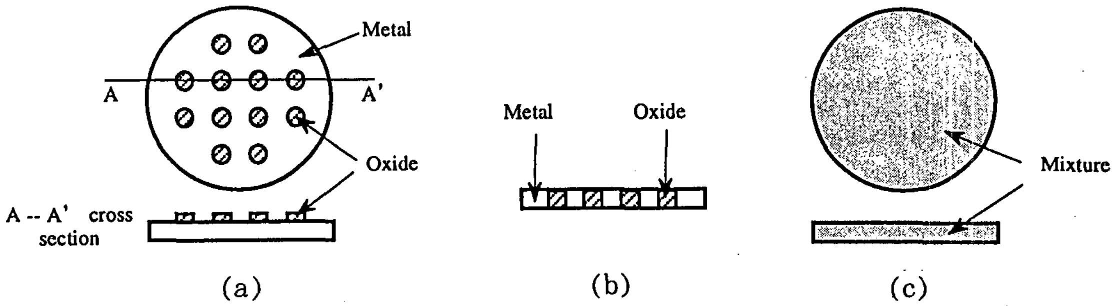


Fig. 3. Explanation diagram of (a)metal-ceramic composite target, (b) composite target with imaginry hole and (c) mixture target consisted of Zr, Ti, and PbO powder.

smashed, mixed and caked, which should be of the dimilar function to Fig. 3(a) or Fig. 3(b). According to the imagination, it is considered feasible to fabricate the mixture target as in Fig. 3(c) using Zr, Ti, and PbO powder. Therefore, (ZrTi+$x$PbO) powder target with the same $x$ as that of the composite target is used to prepare PZT film. The sputtering ch-amber was evacuated to a background pressure less than $1\times10^{-6}$ Torr. Argon gas (6.9sccm) was introduced into the chamber, keeping the pressure of 10m Torr by throttling the main valve. The target was pres-puttered to clean with a shutter closed for 45min before introducing oxygen into the system. Typical sputtering conditions are tabulated in Table 1.

Table 1. PZT thin film sputtering conditions

| | |
|---|---|
| target | ZrTi(50%/50%)<br>(Purity : 99.99%)<br>pbo power<br>(Purity : 99.999%)<br>Zr powder(Purity : 98%)<br>Ti powder(Purity : 98%) |
| RF input power | 200W |
| Substrate temperature | 190℃ to 600℃ |
| Ar gas pressure | 10mTorr(6.94sccm) |
| Sputtering gas | $Ar+O_2$ |
| Substrate | Fused quartz glass<br>$Pt/Ti/SiO_2/Si$ |
| Target-substrate distance | 62mm |

The crystalline structure of the films was examined by an X-ray diffraction (XRD) method. The film composition was analyzed by an electron probe microamalysis (EPMA) method. Depth profiles of the deposited films were observed by secondary ion mass spectroscopy (SIMS). The ferroelectric properties of the PZT films were measured using Radiant Technologies model RT66A ferroelectric test equipment.

## RESULTS AND DISCUSSION

**Fundamental properties**

To investigate the fundamental characteristics of the reactive sputtering using the (ZrTi + $\chi$PbO) composite target, we measured the deposition rate with changing $O_2$/Ar flow rate ratio and $\chi$ at a substrate temperature of 190℃ using fused quartz glass substrate, and the results are shown in Fig. 4. Only with the PbO ceramic trget, the deposition rate was about 35 nm/min and hardly dependent on $O_2$/Ar flow rate ratio. On the other hand, only with the ZrTi alloy target, when

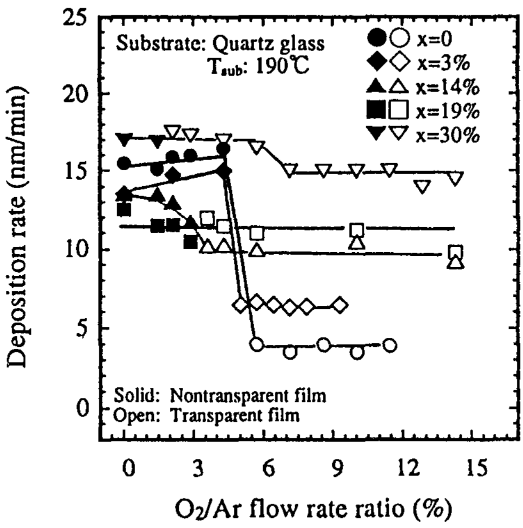


Fig. 4. Deposition rate dependences on $O_2$/Ar flow rate ratio using (ZrTi+ $x$PbO) composite target.

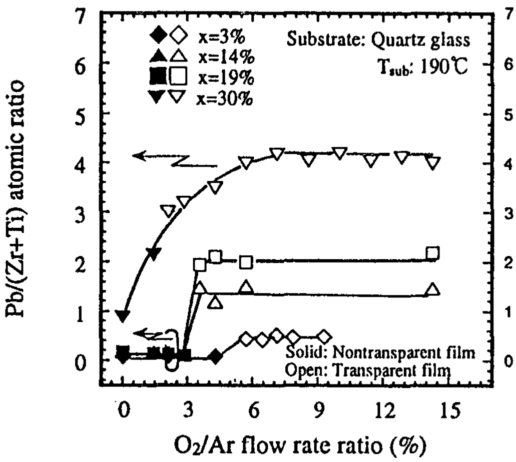


Fig. 5. Pb/(Zr+Ti) atomic ratio as a function of $O_2$/Ar flow rate ratio and PbO area ratio ($x$).

$O_2$/Ar flow rate ratio is lower than 5%, the target surface was kept metallic mode condition and nontransparent metallic films were deposited. With higher $O_2$/Ar flow rate ratio the target surface was kept oxide mode condition and transparent oxide films were deposited. It is seen from Fig. 4 that the transition point between the two operation modes shifts to lower $O_2$/Ar flow rate ratio as x increases up to 14%. With increasing $\chi$, deposition rate decreases in the metallic mode, while it increases in the oxide mode. Finally, the deposition rate becomes almost the same for the two modes at $\chi=19\%$, hence, a transition point cannot be found. However, when $\chi=30\%$, in the region corresponding to the metallic mode, the deposition rate becomes higher than that for only the ZrTi target and transparent oxide films are obtained even in the region corresponding to the metallic mode. It is considered that the PbO molecules of high sputtering yield are sputtered with ZrTi atoms, and oxygen is provided from the PbO.

In order to clarify the details, the above film composition was analyzed by the EPMA method and the results are shown in Fig. 5. Even up to $x=19\%$, distinct and abrupt transition points are observed by this method. However, when x increases to 30%, the Pb/(Zr+Ti) atomic ratio increases gradually with $O_2$/Ar flow rate ratio up to 7% and then becomes constant.

We consider that, as $O_2$/Ar flow rate ratio increases, the ZrTi target surface is oxidized gradually so that oxygen gas increases due to decrease of gettered oxygen, and consequently,oxidization is easier on the substrate. We define it as quasi-metallic mode. In the mode, because Zr and Ti metal atoms arrive on the substrate surface and react with oxides and oxides and oxygen, deposition rate of oxide films is higher than of metal.

## Film structure

### X-ray diffraction

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 structure of various films prepared by changing the target and the substrate temperature is analyzed by XRD method and summarized in Fig. 6. At 450℃, the films exhibit the pure perovskite PZT phase. The temperature range in which the pure perovskite phase is obtained becomes wider as $x$ =24%, however, the pure perovskite PZT phase is not obtained. Therefore, the supply of excess Pb favors perovskite-phase formation.

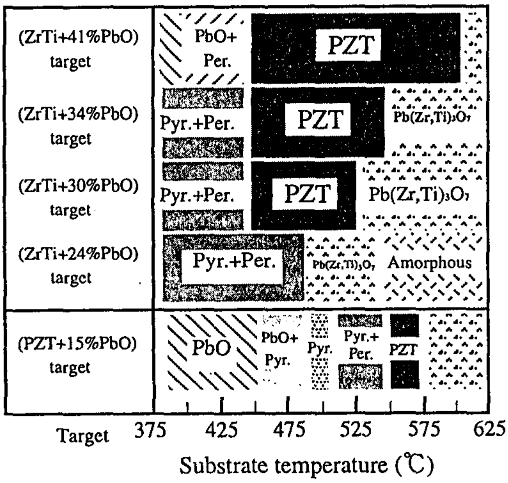


Fig. 6. Crystalline structure of the films prepared in the quasi-metallic mode as a function of growth temperature and target structure.

For comparison with the (ZrTi+PbO) target, the films were also prepared using the (PZT+15%PbO) ceramic target. It was found that perovskite PZT films were obtained only in the narrow temperature range from 540℃ to 570℃.

SIMS depth profiles

To examine the interfce 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. 7(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 te underlying electrode. Interdiffusion between the PZT film and the substrate and mixing are enhanced with increasing growth temperature, as shown in Fig. 7(b) for 525℃ and Fig. 7 (c) for 570℃. Marked damage is observed in the underlying electrode rather than in the PZT film, especially the underlying electrode at 570℃. Therefore, the low temperature process is useful not only for the formation of an abrupt PZT film-electrode interface but also a reliable electrode.

**Quasi-metallic mode of powder target**

In the reactive sputtering using the composite target, as shown in Fig.4 and Fig. 5, it is found that there is a low-temperature and

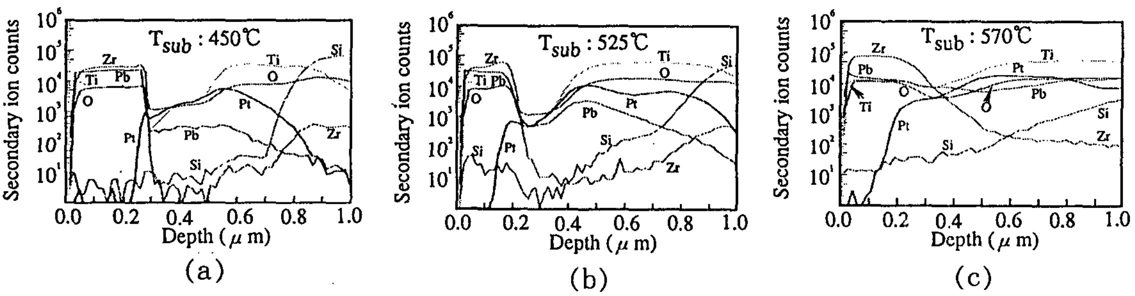


Fig. 7. SIMS depth profiles of the PZT films prepared at (a) 450℃, (b) 525℃ and (c) 570℃.

high-rate mode defined as quasi-metallic mode. However, because the target structure is unstable, it is not useful in practice. We speculated that film deposition in quasi-metallic mode could be realized using Fig.3(c) target. Therefore, the fundamental experiment was investigated using the (ZrTi+30%PbO) powder target. In order to investigate if the quasi-metallic mode can be realized or not, the film properties prepared using the target are compared with those using the composite target.

### $O_2$/Ar flow rate ratio dependence

Because the pure perovskite phase was obtained in the quasi-metallic mode at the growth temperature of 450℃ as shown in Fig. 4, we selected 450℃ to investigate $O_2$/Ar flow rate ratio dependence. At $O_2$/Ar=1.15 %, a mixture of pyrochlore and perovskite phases is observed. In the $O_2$/Ar flow rate range from 2.1% to 4.3%, pure perovskite PZT films are obtined also, which is the similar to that for the composite target. At higher $O_2$/Ar flow rate ratio, mixture of PbO, pyrochlore and perovskite PZT phases is obtained. Figure 8(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 pttern of the film prepared in the oxide mode at $O_2$/Ar=1/1.

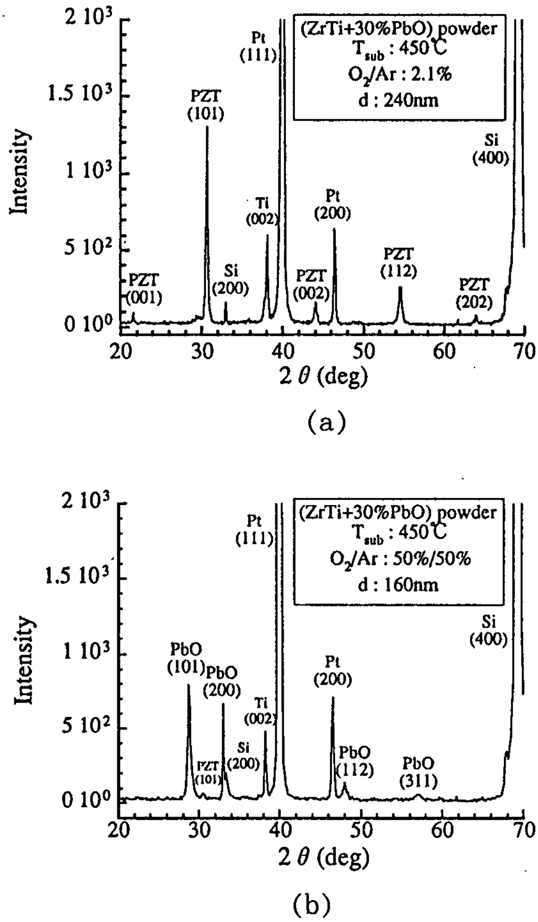


Fig. 8. XRD patterns for the (ZrTi+30%PbO) powder target
(a) in quasi-metallic mode ($O_2$/Ar=2.1 %) and
(b) in oxide mode ($O_2$/Ar=1/1).

### Electrical properties[7]

To examine the electrical properties of the films, Au upper electrodes with 300㎛ diameter were evaporated on the PZT films. Figure 9(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㎛/㎠ and the coercive electric field Ec of 150kV/cm, and (b) does the result of the PZT film prepred using the (ZrTi + 30 % PbO) powder target at 450℃ with the Pr=31㎛/㎠ and Ec=130kV/cm, which shows better electrical performnce.

### Mixture target proposition

For ferroelectric, piezoelectric films and metal oxide deposition using sputtering method, the metal target or the ceramic target is

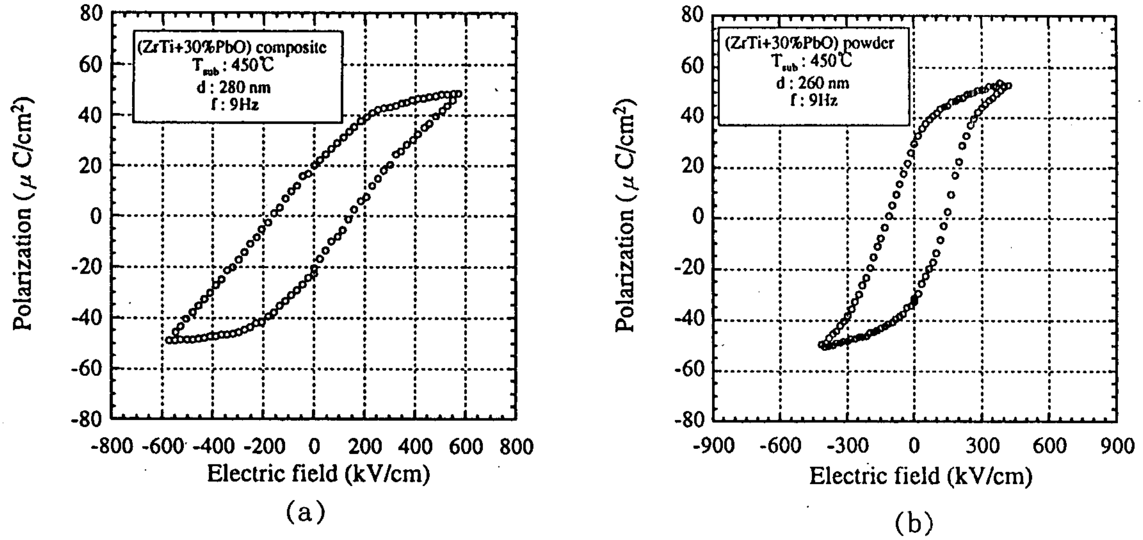


Fig. 9. P -E hysteresis characteristics at the growth temperature of 450℃ for (a) the composite target and (b) the powder target.

usually used. However, by reactive sputtering using the metal target, deposition rate is low in the oxide mode and the reaction control is difficult. On the other hand, although good films can be prepared using the ceramic target, there is radiation damage on the films from negative ions and high-energy neutrals. Moreover, for the both targets, reaction occurs on the targets and then the oxides are sputtered on the substrate.

In this report, we propose a mixture target of metal oxide. Using the target in quasi-metallic mode, reaction occurs on the substrate surface and the deposition rate is higher than of only metal target. Therefore, low temperature fabrication is possible and an epitaxial growth will become easier. Because of the high rate, it is unnecessary to use a magnetron sputtering, which is beneficial to the target recycle. Examples of the mixture target composition are tabulated in Table 2.

Table 2. Mixture target examples

| Deposition film | Target |
|---|---|
| PZT | Zr-Ti-PbO |
| ZnO | Zn-Zno |
| $LiNbO_3$ | Li-Nb-$Li_2O_2$ |
| ITO | In-Sn-$SnO_2$, In-Sn-$In_2O_3$ |
| YSZ | Zr-$Y_2O_3$ |

## CONCLUSIONS

PZT films were prepared by conventional rf diode reactive sputtering using (ZrTi+$\chi$ PbO) composite target. At $\chi \geqq 30\%$, PZT films were obtained at $O_2$/Ar=2.1% with high rate that is almost equal to that of metallic mode. We defind the mode as the quasi-metallic mode. However, because the target structure is unstable, it is not useful in practice . In order to overcome the disadvantage, 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 the similar to that prepared using the composite target could be obtained. Therefore, the mixture target was proved efficient. The method can be applied for various metal oxide and composite film preparation. Moreover, because reaction occure on the substrate surface, it is considered that this method is effective for laser ablation and reactive evaporation *et al.* also.

## ACKNOWLEDGMENTS

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