Growth of piezoelectric thin films by sputtering

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ABSTRACT

Lead titanate thin films have been deposited on different substrates by radio frequency magnetron sputtering from pressed powders targets. The films have been deposited without substrate heating. The amorphous films were then annealed in order to obtain the perovskite structure. Two types of post-annealing were study : conventional annealing and rapid thermal annealing (R.T.A.). The main advantage of the RTA process is to avoid (or to limit) the problem of interdiffusion or of interfacial disturbance between the substrate (in particular Silicium substrate) and the lead titanate thin film. The composition, structure and microstructure of PT films were evaluated as a function of the annealing parameters for conventional and rapid annealing.

1- INTRODUCTION

Lead titanate (PT) is a well known ferroelectric material showing large piezoelectric, pyroelectric and electro-optic effects. Recently considerable attention has been focused on piezoelectric thin films because of their many possible applications to electronic, optoelectronic and integrated devices. Several techniques such as evaporation¹, R.F. sputtering², ion beam sputtering³, laser ablation⁴, sol-gel⁵ and chemical vapor deposition⁶ (CVD) have been employed in the preparation of piezoelectric thin films (PZT, PLZT, ...). R.F. sputtering is a well suited method to grow ferroelectric thin films at very low temperature⁷.

We have performed a series of experimental trials for developing radio-frequency sputtering fabrication and post-annealing treatment technology of PT thin films grown on different substrates.

2- EXPERIMENTAL DETAILS

A radio-frequency (R.F.) magnetron sputtering system, described previously⁸, was used to prepare PT thin films. The sputtering target was a mixture of PbO and TiO₂ powders (purity 99,9 %) uniaxially cold pressing. Such a target is quick and inexpensive to prepare and usable for many runs. The target diameter and thickness are 25,4 mm and 2 mm respectively.

In order to obtain the film stoichiometry, with our sputtering conditions, we have used targets of composition $x\text{PbO} + \text{TiO}_2$ with $x = 0,54$. The principal reason is that the sputtering yield of Pb is much higher than that of Ti in general⁹. The sputtering conditions used in this experiment are summarized in table I. Deposition were performed at room temperature and the process gas is pure argon. The growth rate is in the order of 720 Å/h on silicon substrate ; it is more important on sapphire substrate (1080 Å/h).

R.F. Power	10 W
Interelectrode distance	35 mm
Sputtering gas	Ar
Gas Pressure	100 mT
Substate Temperature	Ambiant

Table I

The PT films were deposited on different substrates : (0112) and (0001) sapphire, oxidized (100) -n - Silicon (Si) wafers and (100) - n - oxidized Si with thin Ti/Pt alloy layer. The PT film thickness is 3000 Å (measured by profilometry : alpha step 200 TENCOR). The post-annealing treatments were made by conventional furnace annealing (horizontal quartz tube) or rapid thermal annealing (Jipelec Jetstar 4¹⁰) in air. The crystal structure and thin films composition were analyzed by X-ray diffractometer and ICP (Inductively Coupled Plasma) respectively. Scanning electron microscopy (SEM) was used for microstructural characterization.

3- RESULTS AND DISCUSSION

3-1 Conventional annealing

The films present an excess of Pb just after the growth ; the (Pb/Ti) ratio of the films was equal to 1,15. We have voluntarily conserved such a Pb concentration in the film since the growth were made on unheated substrates and so the films were amorphous. A post-deposition annealing was necessary to induce crystallisation in the as grown films and during this treatment PbO lost from the film.

We have evaluated the lost of PbO for PT films grown on Al₂O₃ substrates. PbO loss as a function of annealing temperature is shown in fig. 1. The annealed time was fixed to 2 hours. Since the vapor pressure of PbO increases with temperature, the loss of PbO increased with annealing temperature. There is no PbO evaporation below an annealing temperature of 600°C. At 680°C, the loss of PbO is nearly equal to 14 %. The same behaviour is observed for films which contain an important excess of Pb (Pb/Ti = 2,3). As we can observed the loss of PbO due to evaporation increases with increasing PbO content in the as-deposited films : at 680°C the loss of PbO is 22 %. In comparison, it has been reported that PbO evaporation begins at approximately 600°C in bulk PbTiO₃ samples¹¹. Initial film composition has a little effect on the temperature necessary for PbO evaporation, but it has a significant influence on the slope of the line relating loss to annealing temperature.

Fig. 2 shows the loss of PbO as a function of annealing time ; the annealing temperature is maintained at 680°C. For 15 min and 30 min annealing time there is no PbO evaporation, it begins at approximately 1 hour (~ 4 %). On Si/SiO₂ substrate, a similar behavior is observed. Films composition with high PbO excess exhibit PbO evaporation at 30 min.

So, we can conclude that for films with an as-deposited composition of Pb/Ti = 1,15 a post-deposition annealing at 680°C during 2 hours is necessary to have a Pb/Ti ratio equal to 1.

With these annealing parameters, optimized for films composition we must examine the crystallographic structure and the microstructure of PT films.

fig.1

fig.2

As deposited thin films produce X-ray diffraction patterns consistent with an amorphous structure. The effect of annealing temperature on crystallization is presented in fig. 3 for films with a starting composition of $(\text{Pb/Ti}) = 1,15$ grown on (0112) Al_2O_3 substrate, the annealing time is 2 hours. The perovskite structure is initiated at a temperature as low as 450°C ; it is well known that an excess of PbO favors the perovskite phase formation. The crystallinity of the film increased when the annealing temperature increased, evidenced by higher and sharper XRD peaks. The crystallisation is completed at 680°C , the tetragonality of the PT film is $c/a = 1,057$. For higher temperature (700°C) the XRD peaks intensity decreased.

It is interesting to note that crystallization and PbO loss begin at about the same temperature, implying the interdependence of these two diffusion-controlled processes. Fig. 4 shows the evolution of the crystallisation with the annealing time; the annealing temperature is 680°C . 15 min. annealing time is sufficient to initiate the perovskite structure; we can observe an improvement of the crystallinity of the film when the annealing time increased. The PT films have a (101) preferred orientation on (0112) Al_2O_3 substrate.

We have made a similar study on (0001) Al_2O_3 substrate; the results are presented fig. 5. The (101) preferred orientation is also observed.

fig.3

fig.4

fig.5

The annealing parameters : 680°C during 2 hours are also perfectly well adapted to Si/SiO₂ and Si/SiO₂/Ti/Pt substrates as we can observed fig. 6.

The surface morphology of PT films was observed with a scanning electron microscope (SEM).

Fig. 7 shows the SEM picture for the PT film on Al₂O₃ substrate after it was subjected to furnace annealing to 680°C for 2 hours. The film have a dense morphology without porosity. Fig. 8 shows the SEM observation of the edge of a Si/SiO₂/PT sample, obtained by simple cleaving, before and after annealing at 680°C during 2 hours (fig. 8a and 8b respectively). After annealing, the columnar structure disappear and the film is well densified.

fig.7

fig.8-a

fig.8-b

The inconvenience of such annealing treatment is the high annealing temperature which is not always compatible with semiconductor processing. Therefore, efforts have been made to reduce the processing temperature or the annealing time.

In this practice, rapid thermal annealing (RTA), initially used in semiconductor technology has been shown to be a suitable technique to crystallize ferroelectric thin film^{12, 13}.

RTA, with radiations from halogen lamps, has advantage over conventional furnace annealing to much shorter annealing times necessary to crystallize and so to minimized film-substrate interface reactions.

3-2 Rapid thermal annealing

We have studied the influence of the annealing parameters on PT films crystallization. The RTA system used in this work was a commercial JETSTAR 4 manufactured by JIPELEC. The initial composition of films is given by $\text{Pb/Ti} = 1,15$; the film are grown on Al_2O_3 substrates. An important property of the RTA, by comparison with conventional annealing, is to lower the crystallisation temperature. Firstly, we have determined the annealing temperature necessary to crystallize the film when the annealing time is fixed to 30 s. Fig. 9 shows that at 500°C the perovskite structure is present without any second phase (in particular pyrochlore phase).

At 600°C (fig. 10) the crystallinity of the film is improved (higher XRD peaks). At higher temperature any improvement was observed. The degree of crystallinity (peaks intensity) is the same to that obtained during 30 min. at 680°C by conventional treatment.

When the annealing time is reduced, the annealing temperature must be increased. For example for an annealing time of 5 s, the annealing temperature at which the perovskite structure is well defined was 680°C (fig. 11). The tetragonality of the PT film is $c/a = 1,062$ (the theoretical value is 1,063).

Fig. 12 shows the microstructure of a PT film annealing by RTA (680°C - 30 s) ; the annealed film attained a dense morphology without porosity and a very fine grain size. It is directly related to the fast firing ; this treatment improved the densification and limited the grain growth. Further studies were investigated to optimize the process.

fig.12

4- CONCLUSION

PT films have been obtained by a sputtering technique with a post-deposition conventional or rapid thermal annealing treatment.

The conventional thermal process has been optimized in terms of composition, structure and microstructure on different substrates.

By rapid thermal annealing, the structure is completed at 600°C for 30 s without pyrochlore phase. In conventional annealing, the temperature to obtain the perovskite phase is about 680°C and an annealing time of about 2 h is necessary to complete the crystallisation. These results confirm that rapid thermal processing is a very promising technique for fabrication of PT films (or other piezoelectric thin films).

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