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Single-Target Sputter Deposition and Post-Processing of Perovskite Lead Titanate Thin Films

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Abstract

The growth of ferroelectric lead titanate (PT) thin films by RF magnetron sputtering using a single mixed-oxide target is described. This study has been focused on producing perovskite thin (2000 Å) films with the desired composition on different substrates. Depositions were performed at room temperature and the process gas is pure argon. The effects of deposition and post-annealing conditions on film composition and microstructure were evaluated. Optimization of process conditions is discussed in terms of stoichiometry, structure and reproducibility. The optical properties of the films have also been characterized.

In der vorliegenden Arbeit wird die Herstellung dünner ferroelektrischer Bleititanatfilme (PT) beschrieben, die aus einer einzelnen Probe, bestehend aus verschiedenen Oxiden, mit Hilfe von RF Magnetronsputtering gewonnen wurden. Die Untersuchung konzentrierte sich hauptsächlich auf die Herstellung dünner Perovskitfilme (2000 Å) gewünschter Zusammensetzung unter Verwendung verschiedener Substrate. Die Aufbringung erfolgte bei Raumtemperatur mit Argon als Prozeßgas. Der Effekt der Aufbringungs- und der Anlaßbedingungen auf die Filmzusammensetzung und die Mikrostruktur wurde untersucht. Die Optimierung der Prozeßbedingungen wird bezüglich der Stöchiometrie, der Struktur und der Reproduzierbarkeit diskutiert. Desweiteren wurden die optischen Eigenschaften der Filme bestimmt.

Nous décrivons dans cet article la croissance de couches minces ferroélectriques de titanate de plomb (PT) par pulvérisation cathodique RF magnétron à partir de cibles d'oxydes. L'objectif est la réalisation de couches minces (2000Å) de $PbTiO_3$ possédant la structure perovskite sur différents types de substrats. Les dépôts sont réalisés à température ambiante, le gaz de décharge est de l'argon pur (sans ajout d'oxygène). Les conditions de dépôts et de recuits sur la composition et la microstructure des couches sont étudiées et optimisées. Nous avons également caractérisés les propriétés optiques des couches minces.

1 Introduction

Perovskite ferroelectric ceramics have been receiving much attention due to their excellent functional properties, such as piezoelectricity, pyroelectricity, electrooptic effect, and so on. A number of devices have been proposed;[1,2] however, the use of bulk ceramics has been limited by the relatively high switching voltages required. The progress made in depositing high quality, very thin ferroelectric film has opened a new area for applications in microelectronics, especially their possible integration with silicon technology. There are different techniques, eg. evaporation,[3] ion-beam deposition,[4] some chemical routes employing sol–gel techniques,[5,6] laser ablation[7] and chemical vapour deposition[8] for the fabrication of these films. Two considerations essential for development of this new technology are the fabrication procedure and the selection of materials. Sputtering is a physical processing method well suited for the formation of thin layer ceramics,[9,10] but in order to utilize its full potential many processing variables must be considered. In terms of materials, lead titanate (PT), lead zirconate titanate (PZT) and lead lanthanum zirconate titanate (PLZT) provide a particulary versatile choice.

In the present paper the authors report on the growth, the composition and the structural characterization of PT thin films deposited at room temperature from an oxide target by RF mag-

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netron sputtering. Two types of oxide targets were studied and the effects of the target on the composition and the structure of PT films have been analysed. Primary factors in the synthesis and crystallization of PT thin films are a good control of the deposition kinetics and the lead (Pb) content of the film. The latter can vary widely, due to the particular chemistry of this element and to the fact that the sputtering yield of Pb is much higher than that of Ti in general. Sputtering and annealing conditions have to be optimized in order to obtain the perovskite structure on sapphire and silicon substrates.

2 Experimental

2.1 Sputtering equipment

In this section the sputtering equipment and its operation will be described. Thin films of PT have been fabricated using RF magnetron sputtering with an horizontal cathode. The substrate temperature varied between room temperature (water-cooled substrate) and 750°C, and was detected by a thermocouple placed just behind the substrate. In this study, the depositions were made at room temperature; more precisely it has been observed that, without heating, the substrate temperature reaches about 50°C during the deposition procedure (ion bombardment) for the present sputtering conditions (see later).

The substrate block was suspended from an horizontal bar and could be conveniently moved to vary the substrate to target distance between 20 mm and 80 mm. The system is equipped with three cathodes; their diameters varied between 1" and 3". The substrate block can be rotated to place the substrate in front of the target. In order to stabilize the surface of the target a presputtering is necessary. For this purpose, a shutter (between the target and the substrate) is used for presputtering of the target just before the growth of the film. It has been observed that several hours at low (gradually increasing) power is suitable to form the 'altered layer' on the surface of the target. This layer acts to maintain proper bulk stoichiometry in the sputtered atoms even if the sputtering probabilities of the constituents differ.[11] Typically the system was pumped down to a base pressure of 1×10^{-7} mbar before introducing argon and/or oxygen into the system. In these experiments, depositions were made in pure argon. The sputtering pressure was controlled using a capacitance nanometer. An automatic 300 W RF power supply, capable of operating in a constant voltage, current, or power control mode was used.

2.2 Substrate

The PT thin films were deposited onto different substrates: (0112) sapphire, oxidized (100) silicon (Si) wafers and (100) oxidized Si with a thin sputtered Ti–Pt alloy layer. The Ti–Pt (film thicknesses were 500 Å and 1000 Å respectively) films were deposited on the substrate as base electrode mainly because of its superior barrier effect against chemical reactions and its better adhesion to Si oxide than Pt alone. Pure Pt film has such weak adhesion to Si oxide that the film is easily peeled off after the PT film is deposited. The substrate nature had an important effect on crystallisation behaviour of the films.

All substrates were thoroughly cleaned in a series of organic solvents and deionized water prior to film deposition. The silicon wafers were etched away in hydrofluoric acid prior to chemical cleaning.

2.3 Target

The effect of the target material on the structural of radio frequency sputtered $BaTiO_3$ films has been reported.[12] Here the influence of a single composite oxide target on the composition and the structure of the PT films has been studied.

Two types of oxide powder targets were used:

—A mixture of PbO and TiO_2 powders (purity 99·9%). The target compositions are given by the formula: (x PbO + TiO_2) where $x \leq 1$.

—$PbTiO_3$ reacted powder prepared in the standard way[13] from PbO and TiO_2 powders by mixing and grinding followed by firing for 6 h at 650°C in O_2 flow, followed by a slow cooling to room temperature. The resulting powder was then reground.

In the two cases, the target diameter was 25·4 mm; they were obtained by uniaxially cold pressing, the final thickness being 2 mm. The composition of the target material was analysed by inductively coupled plasma (ICP), the ratio (Pb/Ti) is 1. X-Ray measurement revealed the quadratic single-phase structure (for the $PbTiO_3$ reacted powders).

As has been mentioned previously a presputtering run is necessary to form the 'altered layer' but also to outgas the target (adsorption). The gradual release of residual trapped gas from such a powder target is unlikely to be a problem for this oxide material. With care, the targets remained stable, without cracking or otherwise degrading, for up to many deposition runs (40 h). The advantages of such a target include convenient and rapid adjustment of target composition as well as economy.

2.4 Thin film characterization

The thickness of the $PbTiO_3$ films was measured by profilometry (alpha-step 200, Tencor instruments); the film was then chemically etched (hydrochloric acid) to make a step between the film and the substrate. The composition of the films was determined by ICP. The structure and the preferred orientation of the films was examined by X-ray diffraction (XRD) while the film morphology and the grain size was examined using a scanning electron microscope (SEM). The optical properties of the films were investigated in terms of optical transmission.

3 Results and Discussion

3.1 Deposition rate and composition

Sputtering conditions such as power, sputtering pressure, gas composition and substrate temperature are known to affect the deposition rate and the film composition. The parameters which have to be selected in the present study were: target material, RF power, gas pressure and distance between target and substrate.

The substrate temperature was kept at room temperature to improve control over composition, mainly concerning the lead content. Pure argon was used as sputtering gas; it has been observed that mixing oxygen in argon induced a drastic drop in deposition rate and increased the roughness of the film surface.[14] The deficiency in oxygen is supplied by post-deposition annealing of the film. Figure 1 shows the variation on the deposition rate versus RF power for a film grown on sapphire substrate; the sputtering pressure P was fixed to 100 mTorr. The composition of the target (mixture of PbO and TiO_2) was xPbO + TiO_2 with $x = 1$. The deposition rate increased with the RF power, since the ion energies increased. Identical results were obtained for all the substrates and for the $PbTiO_3$ reacted powder target. The composition of the film and more precisely the ratio Pb/Ti is little influenced by the RF power, as can be observed in Fig. 2. The as-deposited films were Pb rich; this effect was more pronounced for the PbO + TiO_2 target: Pb/Ti = 2·5, while it was 1·5 for the $PbTiO_3$ target.

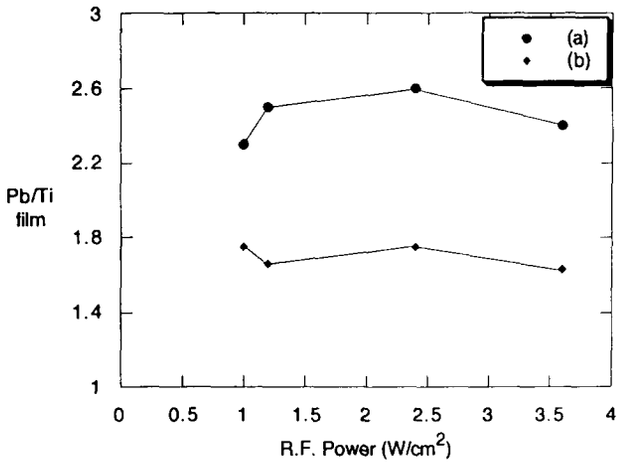


Fig. 2. $(Pb/Ti)_{film}$ versus RF power for Al_2O_3 substrate with P = 100 mT; (a) PbO + TiO_2 target, (b) $PbTiO_3$ reacted powder target.

The deposition rate decreased when the gas pressure in the reactor increased (Fig. 3). The number of collisions increased (and so the mean free path decreased) and the sputtered species rapidly lost their energy. At high pressure the resputtering effect contributed mainly to these effects. The deposition rate was similar for the two types of targets; it was in the order of 10 Å/min for P = 50 mTorr (and d = 30 mm). In a similar fashion the deposition rate decreased when the target-substrate distance increased. Above the thermalization distance, transport is by diffusion and the deposition rate decreased rapidly with increasing target–substrate distance.

This phenomenon is directly related to the thermalization distance. Sputtered species that are ejected from the target undergo collisions during

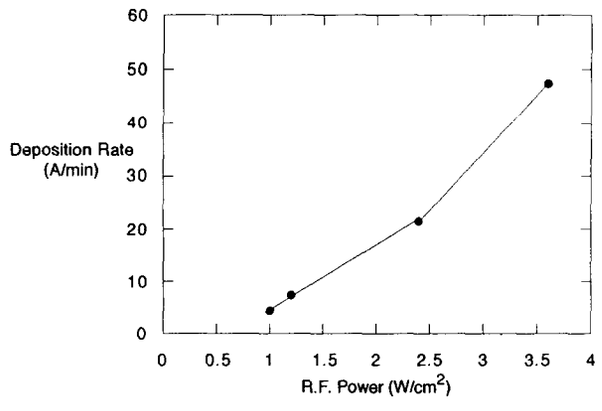


Fig. 1. Deposition rate versus RF power for Al_2O_3 substrate with target composition: PbO + TiO_2; sputtering pressure P = 100 mT.

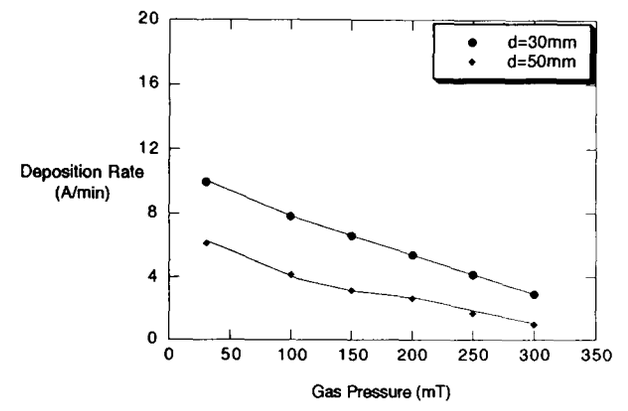
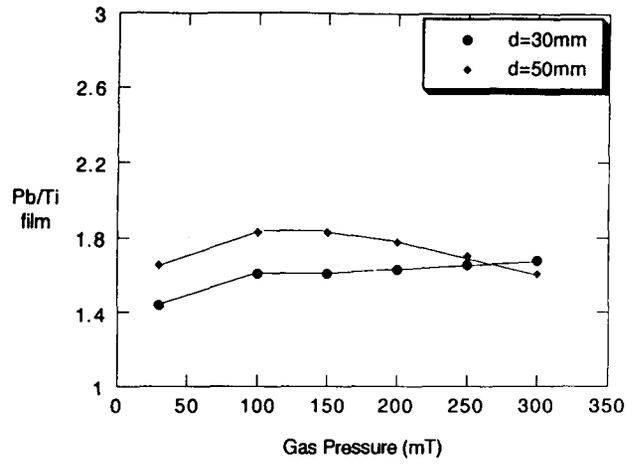
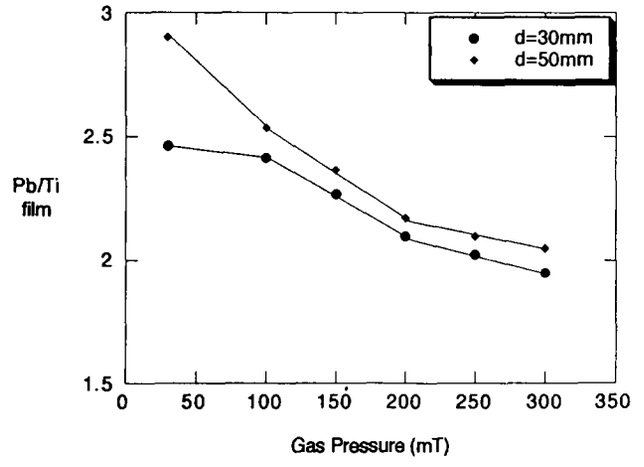


Fig. 3. Deposition rate versus gas pressure (pure Ar) for Al_2O_3 substrate with $PbTiO_3$ target; RF power density = 2·3 W/cm²; d = target–substrate distance.



(a)



(b)

Fig. 4. $(Pb/Ti)_{film}$ versus gas pressure; (a) (b).

transport through the plasma. These collisions serve to thermalize and to mix the ions. Thus a thermalization distance may be defined at a particular sputtering pressure when the kinetic energy of the sputtered particles reduces to values of kT (where k is Boltzmann's constant and T the temperature).

The ratio Pb/Ti varied very little with the gas pressure in the case of a $PbTiO_3$ reacted powder target, the variation was more important for the PbO + TiO_2 target (Fig. 4(a) and (b) respectively). This difference can be attributed to the nature of species which are sputtered from these two types of target. The target–substrate distance was an important parameter to control the film composition; it is essentially due to the resputtering effect.[15,16]

In conclusion, with the present sputtering conditions the films contain an excess of Pb and it is then necessary, to obtain $PbTiO_3$ thin films, to decrease the concentration of Pb in the target. In this context targets of different composition have been realized: x PbO + TiO_2 with $x < 1$. The selected sputtering parameters correspond to a maximum rate, while still avoiding the deterioration of the target: P_{rf} = 2·3 W/cm^2, P = 100 mTorr, d = 30 mm. The results are presented in Fig. 5. For x = 0·45, the suitable film composition has been obtained for all the substrates considered here. Since the films were deposited on unheated substrates they were amorphous and a post-deposition annealing was necessary to induce crystallization in the as-grown films. During annealing treatment, PbO is lost from the film and the losses of Pb have been determined for different annealing temperatures. The post-annealing parameters were : annealed temperature varied between 500°C and 800°C in air, for 2 h. Figure 6 shows the ratio Pb/Ti in the film (sputtered on sapphire substrate) versus annealing temperature. The PbO content in the film was constant between 500°C and 600°C, an important decrease was observed after that. At 680°C, the PbO loss was in the order of 20%. For practical reasons and in particular the technological compatibilities with silicon integrated circuits, the annealing temperature was limited to 700°C. It can be concluded (see Figs 5 and 6) that the target composition must be, with the present sputtering

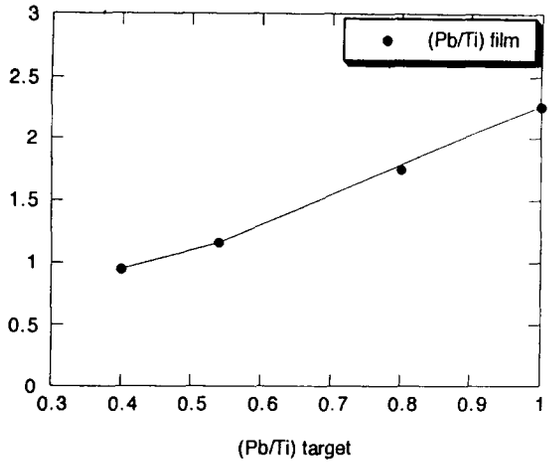


Fig. 5. $(Pb/Ti)_{film}$ versus $(Pb/Ti)_{target}$ on Al_2O_3 substrate. Target = x PbO + TiO_2.

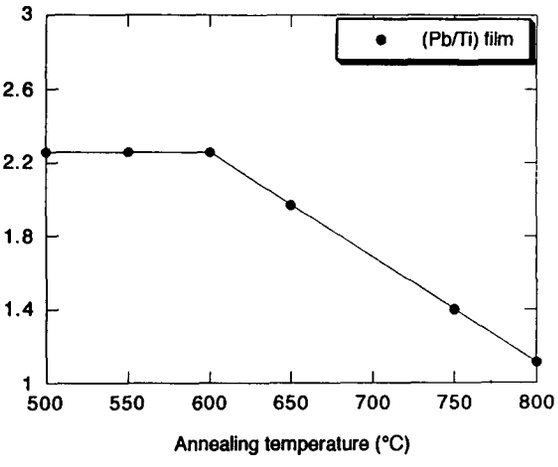


Fig. 6. $(Pb/Ti)_{film}$ versus annealing temperature for Al_2O_3 substrate. Annealing time = 2 h.

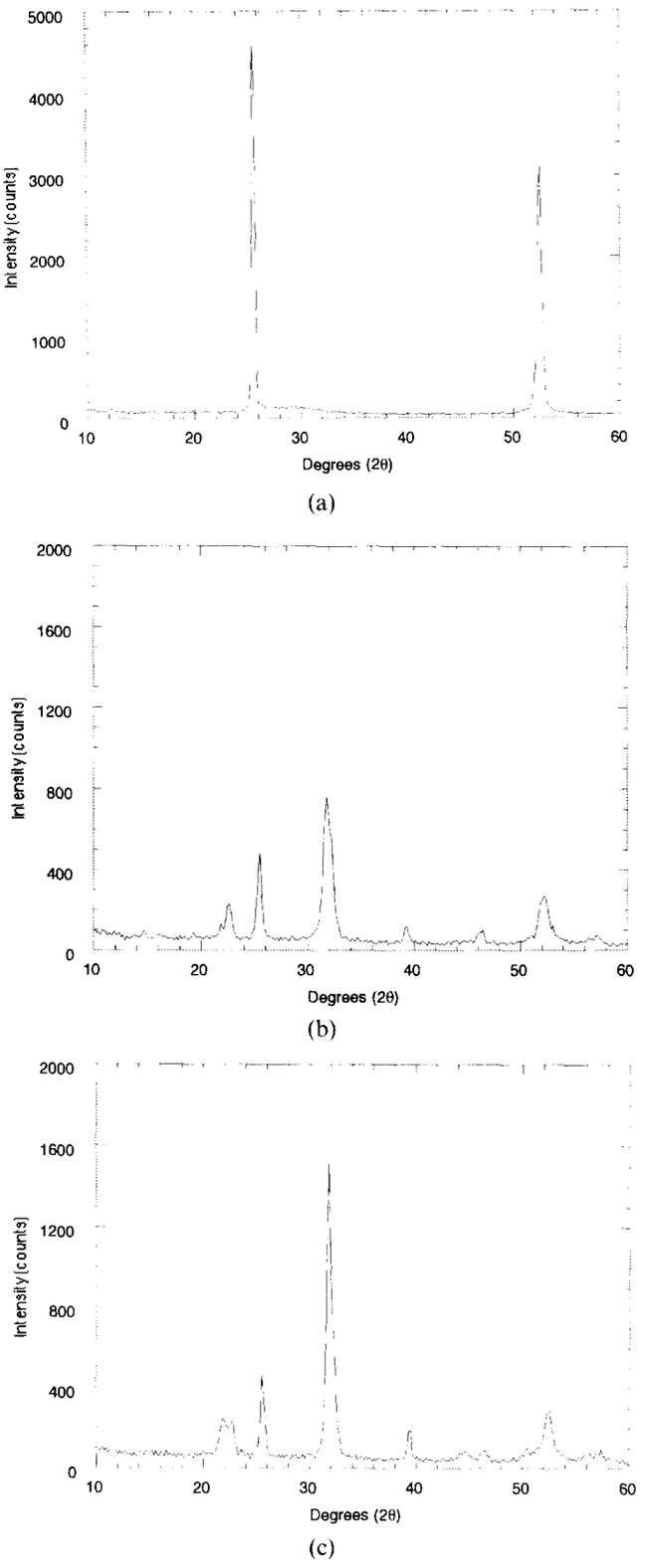


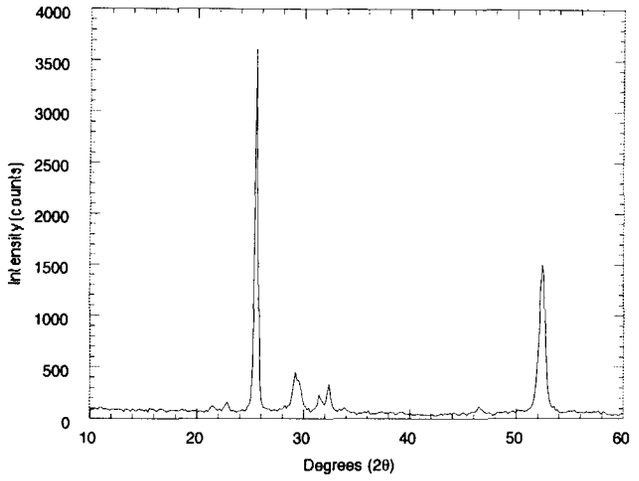
Fig. 7. XRD pattern of PT films with substrate Al_2O_3; target: 0·54 PbO + TiO_2. P = 100 mTorr; d = 30 mm; P_{rf} = 2·3 W/cm^2. (a) As-deposited film; (b) annealing temperature 500°C (2 h); (c) annealing temperature 680°C (2 h).

conditions, 0·54 PbO + TiO_2. It has been verified that with such a target composition and with an annealing temperature of 680°C (for 2 h in air) the Pb/Ti ratio of the film was nearly equal to 1. For the silicon substrates, the PbO loss seems more important, probably due to the formation of lead silicate at the interface between the film and the substrate. With the sapphire substrate the absence of any interdiffusion reaction of PbO in the film limited this effect.

3.2 Crystal structure

The crystallographic structure of the films was examined by standard X-ray diffraction (XRD) methods to determine which crystalline phases were present at various stage of film processing. For this study the film thicknesses were 2000 Å, and they were obtained by sputtering a target of composition: 0·54 PbO + TiO_2 (the growth conditions are indicated on the insert of Fig. 7). In general, the structure of the PT films was observed to be a function of both annealing temperatures, while the annealing time was kept constant at 2 h. Films deposited without substrate heating were amorphous (Fig. 7(a)), at 500°C the crystallization of the films was initiated without second phase (Fig. 7(b)) an improvement of the crystallinity of the film has been observed when the annealing temperature increased, shown by higher and sharper XRD peaks. At an annealing temperature of 680°C (Fig. 7(c)) the film exhibited a pure perovskite phase, the tetragonality of the PT film is (c/a) = 1·057. The crystallites have a random orientation. The c/a ratio of the PT bulk ceramic is 1·063. This small discrepancy is a result of a combined effect of crystallite size and stresses (nonuniform) induced in the film during the growth. It is well known that sputtered films are generally in a state of stress. In this study the case where the film contains, a significant excess of PbO (with a target composition: PbO + TiO_2, Fig. 5) has also been considered. A PbO-rich film favours the perovskite phase formation as can be observed in Fig. 8(a). The perovskite phase appears at 400°C. However, a second phase was observed at 2θ = 29·4°. This peak can be identified with either the massicot or litharge phases of PbO. At 680°C, this second phase is always present (Fig. 8(b)). A longer annealing time is necessary to eliminate the excess PbO. These results indicate that the crystallization of PT films is strongly affected by the Pb content, which is consistent with earlier reports.

The substrate also affects the crystallization. A qualitative comparison among different substrates was made, and the results are presented in Figs 9 and 10 for respectively the Si/SiO_2 and the $Si/SiO_2/Ti/Pt$ substrates (film thickness is 2000 Å; annealing temperature is 680°C for 2 h in air). It has been found that in the order of the substrates of (0112) sapphire, Pt-coated Si is the easiest case in which to achieve the perovskite phase with good crystallinity, while (100) Si/SiO_2 represents the least easy case. The Pt–Ti film thickness was



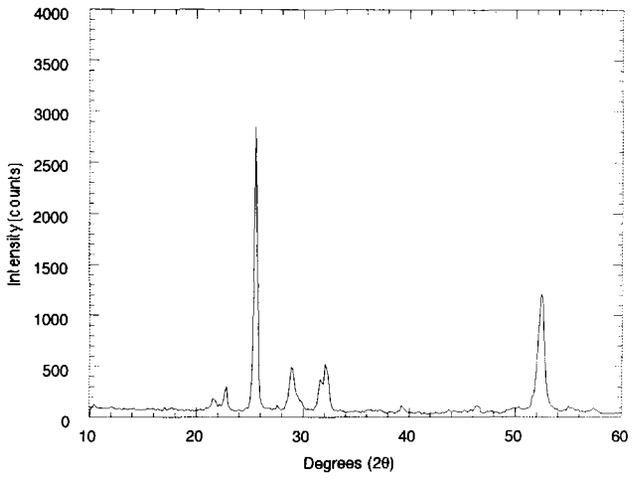


Fig. 8. XRD pattern of Pb-rich PT films with target PbO + $TiO_2Al_2O_3$ substrate. Sputtering conditions identical to Fig. 7. Annealing temperature (a) 400°C (2 h); (b) 680°C (2 h).

found to affect the crystal structure formation. Studies were further extended to explain this behaviour.

3.3 Surface morphology and microstructure

The surface morphology of the deposited film is a determining factor in the use of the material. The surface morphology of as-grown and annealed PT films was observed with a scanning electron microscope. PT films on Al_2O_3 and Pt-coated Si substrates have a very smooth surface with low RMS roughness; after annealing at 680°C to form the perovskite phase, the PT films showed no cracking. On Si/SiO_2 substrates, microcracks were always observed after annealing, probably due to the significant mismatch in the thermal expansion coefficients between the film and substrate. During heat treatment, stress relief occurs and leads to the formation of hillocks or craters. The surface morphology was very rough.

In general, the colour of the as-grown film was a light brown, indicating a slight excess of lead, but after annealing the films were transparent,

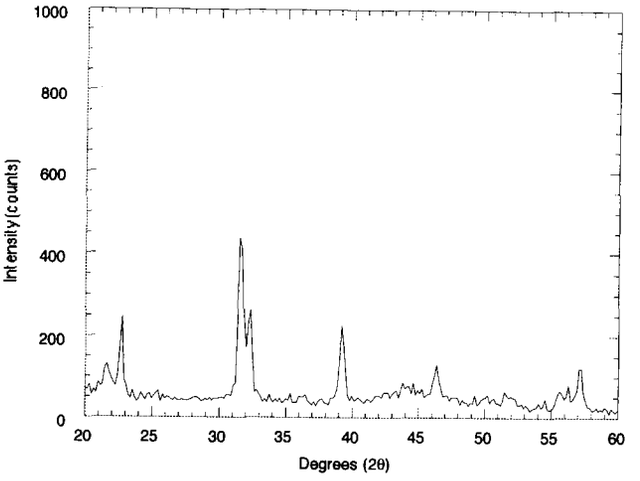


Fig. 9. XRD pattern of PT films on Si/SiO_2 substrate; target: 0·54 PbO + TiO_2. Sputtering conditions identical to Fig. 7. Annealing temperature 680°C (2 h).

with a fine mirror-like surface finish with high optical transparency when examined visually.

It was sometimes observed that with the Pt-coated Si substrates the crystallization of the platinum layer (orientation (111)) results in the formation of pinholes in the PT films.

Figure 11 shows the SEM picture for the PT film on the (0112) Al_2O_3 substrate after it was subjected to furnace annealing at 680°C for 2 h. The annealed film attained a dense morphology without porosity and a very fine grain size. The grain size is calculated from the SEM pictures. The average grain size in the film of 3000 Å is about 80 nm. Identical results were obtained for PT films grown on Si/SiO_2 or $Si/SiO_2/Ti/Pt$ substrates (Fig. 12). It strongly increases with annealing temperature (Fig. 13) and slightly with annealing time. It seems also to depend on film thickness. Further studies are in progress to determine the dependence of the grain on with film thickness.

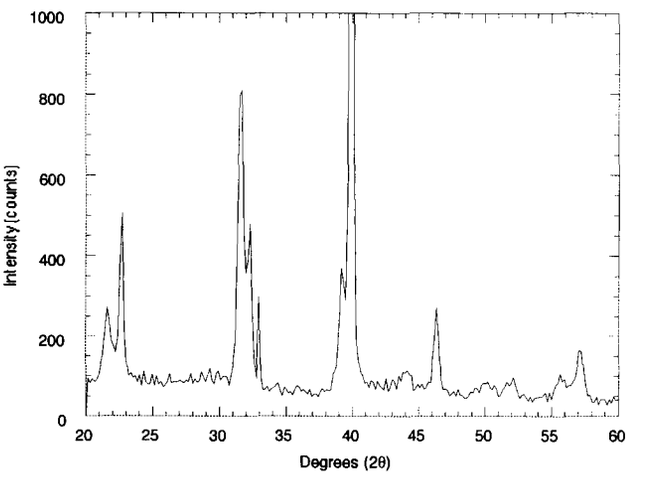


Fig. 10. XRD pattern of PT films on $Si/SiO_2/Ti/Pt$ substrate; target: 0·54 PbO + TiO_2. Sputtering conditions identical to Fig. 7. Annealing temperature 680°C (2 h).

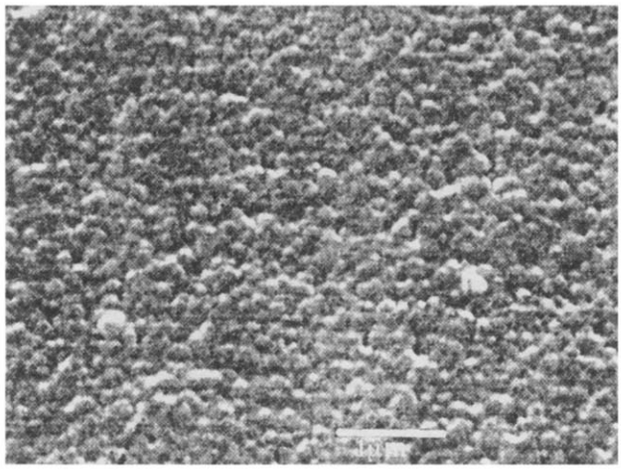


Fig. 11. SEM picture of PT films on Al_2O_3 substrate. Annealing temperature 680°C (2 h).

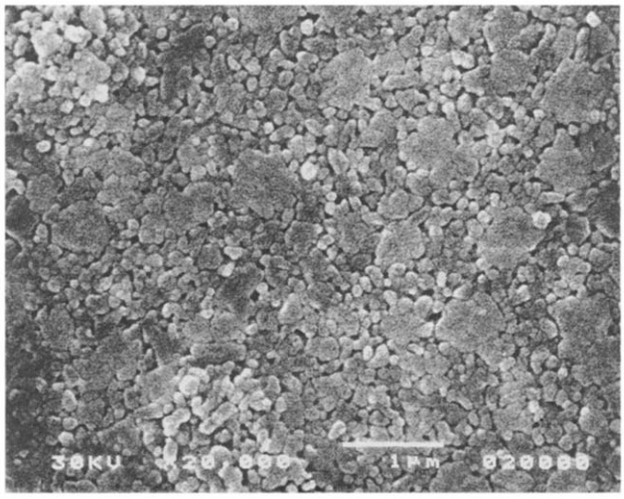


Fig. 12. SEM picture of PT films on Si/SiO_2 substrate. Annealing temperature 680°C (2 h).

3.4 Optical properties

Optical transmittance spectra of the PT films were measured from the ultraviolet to the infrared spectral region. For these measurements, the films were deposited on sapphire substrate (target: 0·54 PbO + TiO_2, the as-grown film contains Pb in excess of 15% (Fig. 5)) and annealed at 680°C for

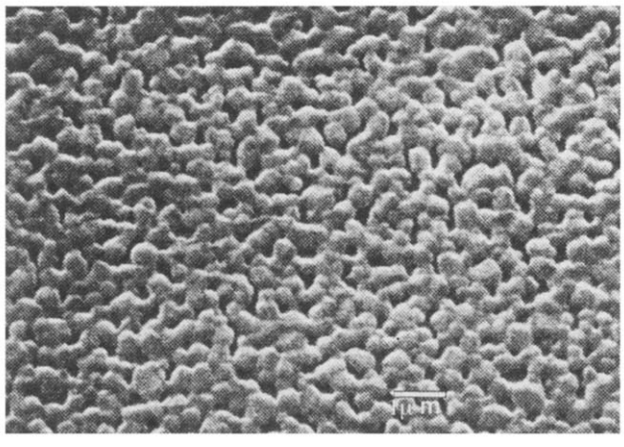


Fig. 13. SEM picture of PT films on Al_2O_3 substrate. Annealing temperature 800°C (2 h).

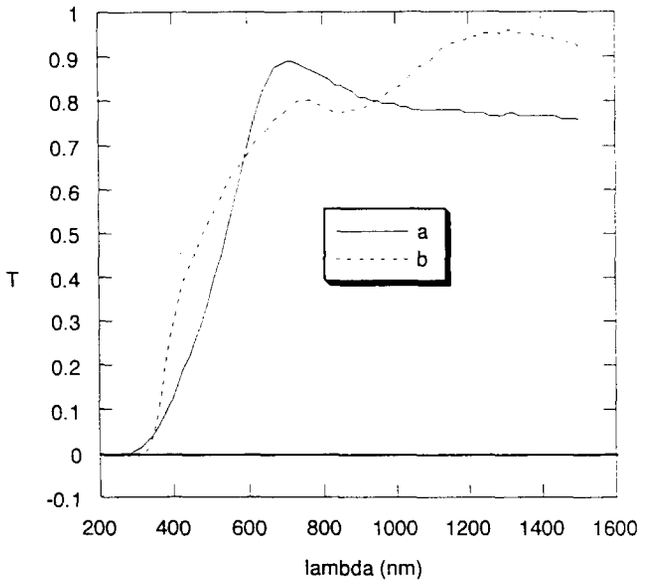


Fig. 14. Optical transmission of PT film; (a) as-grown film, (b) after post-deposition annealing.

2 h. The films are transparent with very low absorption at wavelengths from 400 nm to 1500 nm. As shown in Fig. 14 the average transmission of the PT films (thickness 2500 Å) was about 85% in the infrared region and 70% in the visible region. An absorption edge appears at 400 nm for amorphous films deposited at room temperature. The absorption edge of the films appears at 360 nm after annealing, which is close to the bulk value. Similar shifts of the absorption edge have been reported previously,[17] indicating a change in the chemical composition of the films (decreasing lead content in the films). If the electronic interband transition in PT is expected to be direct, Fig. 14 gives a band gap value of 3·44 eV ($E_g = 1{\cdot}24/\lambda_c$ in eV with $\lambda_c = 360$ nm) for direct transition between valence and conduction bands.

4 Conclusion

PT thin films have been obtained on different substrates by RF magnetron sputter deposition of an oxide powder target: PbO and TiO_2 mixed oxide or $PbTiO_3$ reacted powder. Such a target is quick and inexpensive to prepare and usable for many runs. The sputtering parameters and post-deposition annealing have been optimized for preparing PT films on (0112) sapphire, oxidized (100) Si and oxidized (100) Si/Ti/Pt substrates. The characteristic sputtering conditions were: pure Ar plasma, low substrate temperature (no heating); the target substrate distance was 30 mm. The as-grown films were amorphous. They were transformed to the perovskite structure by a post-deposition annealing. Crystalline phase transformation from an amorphous to a perovskite structure occurs

around 500°C. The PbO content of the film showed an impact on the crystallization in such a way that the presence of excess PbO decreased the temperature of the phase transformation.

The nature of the substrate also showed an influence on the perovskite phase formation; all the substrates exhibited a random orientation. Except in the case of the Si/SiO_2 substrate, the films were very dense. The absorption edge of the films on sapphire substrates was 360 nm. In the infrared region the transmission was about 85%; the films present no cracks and offered a smoother surface.

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