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Kinetics of phase transformations in lead scandium tantalate thin films

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Abstract: The phase transformations from amorphous to pyrochlore to perovskite in lead scandium tantalate (PST) thin films during rapid thermal annealing process (RTA) have been studied. Volume fractions for pyrochlore and perovskite were obtained from their respective X-ray diffraction intensities. Two models assuming the starting phase being pure amorphous or pyrochlore were analysed in detail. Equations have been derived and numerical calculation used to simulate the volume fractions for each phase as functions of annealing time. Transformation parameters k and n were obtained by comparing experiment with simulation using a least-squares curve fitting technique.

Keywords: PST, pyroelectric, phase transformations, kinetics.

AIP classification codes: 77.70.+a, 77.80.Bh, 64.70.Kb.

INTRODUCTION

Lead Scandium Tantalate (PST) is a very promising material in uncooled infrared (IR) radiation sensors for a wide range of applications such as fire alarms, intruder detection and thermal imaging because of its high figure of merit for IR detection. For monolithic IR detectors the thermal budget for PST deposition is limited by the underlying CMOS circuitry which suffers from thermally induced degradation of the Al-Si interconnect metallization [1]. Recently there has been a move away from the fully monolithic approach for PST based detectors in order to remove these thermal budget limitations and enable high merit figures for IR detection to be realized [2]. In this composite thermal detectors the arrays of microbridges are fabricated on an interconnect wafer, able to withstand temperatures of up to 1000 °C, which is then flip-chip bonded to the read-out integrated circuit [2].

Extensive research has been reported on the ordering of PST. However, only limited reports have been devoted to the crystallisation and very little, if any, on the kinetics of phase transformations of perovskite PST from its amorphous or pyrochlore phases. In this paper we report our study on the kinetics of phase transformations from amorphous to pyrochlore and then to perovskite in PST thin films.

EXPERIMENTAL

The substrates used were (100)-Si single crystal wafers which were thermally oxidised and overcoated with a sputtered platinum/titanium(Pt/Ti) layer. The PST was deposited by sputtering. More details have been published elsewhere [3]. The as-deposited wafer was cut into several pieces of squares about 10 mm x 10 mm, and each piece was then subjected to a series of RTA and structural characterisation processes.

RTA of the samples was carried out using an AG Associate Heatpulse system with a heating ramp rate of 100°C/s and natural cooling. A piece of thin film was RTA annealed for a pre-determined time, e.g. 5 s, after the RTA treatment the structures of the film were investigated using conventional $\theta/2\theta$ X-ray diffraction (XRD) scans. This alternating process of RTA and X-ray diffraction was repeated for the same piece of film either until full crystallisation was achieved, or until it was confirmed that no further transformation of pyrochlore to perovskite was taking place.

The Avrami equation [4] has been widely used to model the kinetics of phase transformation and is given by $V(t) = 1 - \exp(- k t^n)$, where $V(t)$ is the transformed fraction at time t, n is the Avrami coefficient whose value normally varies from 1 to 3 [4].

RESULTS AND DISCUSSION

The structure of the as-deposited PST films was found to depend on sputtering conditions especially deposition temperature. Figure 1 shows XRD patterns for the films deposited at 200 (PST499), 300 (PST307) and 450 (PST183) °C respectively. It can be seen that PST183 had strong peaks of pyrochlore. For the film PST499, the crystalline phases included PbO and $Sc_6TaO_{11.5}$, no apparent pyrochlore peaks were observed for this film. For the film PST307 deposited as the intermediate temperature 300 °C, a mixture of PbO, non-stoichiometric $Sc_6TaO_{11.5}$ and pyrochlore $Pb_2(Sc_{0.5}Ta_{1.5})O_3$ were found to co-exist. Apart from these crystalline phases, amorphous material was found by TEM to be present in the films deposited at 300 °C or below.

The complexity of the structure of the as-deposited PST films introduces some uncertainty in the kinetics of the PST crystallisation. For simplicity we consider two extreme cases, i.e., the starting materials being fully amorphous or pyrochlore.

First we consider the starting material being amorphous (model A). Upon annealing PST undergoes transformations from amorphous to pyrochlore (Py) then to perovskite (Pe), which can be represented as follows:

$$x \xrightarrow{k_1, n_1} y \xrightarrow{k_2, n_2} z$$

here x, y, and z are the volume fractions of the amorphous, pyrochlore and perovskite phases respectively, n_1, k_1, n_2, and k_2 are transformation parameters in Avrami equation.

If there is an amount r of the pyrochlore phase which for some reason does not transform into perovskite, then the pyrochlore y can be divided into two parts: an active component y_a, which undergoes the transformation into z and is therefore dependent on all four transformation parameters n_1,k_1,n_2, and k_2, and a passive component y_p which only undergoes transformation from the amorphous but does not convert into z, and therefore is only dependent on parameters n_1 and k_1. The exact time profile of the y_p is not known but it is plausible to assume that this pyrochlore component also obeys Avrami kinetics, i.e.,

$$y_p = r \cdot \left(1 - e^{-k_1 t^{n_1}}\right),$$

then we have

$$y(t) = r \cdot \left(1 - e^{-k_1 t^{n_1}}\right) + \left(1 - r\right) \cdot e^{-k_2 t^{n}} \cdot \int_0^t n_1 k_1 \tau^{n_1 - 1} \cdot e^{-k_1 \tau^{n_1}} \cdot e^{k_2 \tau^{n2}} d\tau \qquad (1)$$

Substituting the expression for y_a to equation (4) gives the following expression for z:

$$z(t) = (1-r)\cdot\int_0^t k_2 n_2 \tau^{n_2-1} e^{-k_2\tau^{n2}} \cdot \left[\int_0^\tau n_1 k_1 \theta^{n_1-1} e^{-k_1\theta^{n1}} e^{k_2\theta^{n2}} d\theta\right] d\tau \qquad (2)$$

where y(t) and z(t) represent the theoretical volume fractions of the pyrochlore and perovskite phases at time t respectively with py and pe the corresponding experimental values. Parameters n_1, k_1, n_2, and k_2 can be obtained by minimising the sum of the squares of the errors (SSE) which was defined as:

$$SSE(n_1,k_1,n_2,k_2) = \sum_i (py_i - Y(t_i))^2 + (pe_i - Z(t_i))^2$$

with summarisation over all the experimental points for the film annealed at a particular temperature.

The volume fractions of the Py and Pe phase (marked by x and ◊ respectively) as functions of annealed time are plotted in figure 2b, theoretical curves of y(t) and z(t) (solid line and dotted-line respectively), as obtained by finding the best fitting parameters n_1, k_1, n_2, and k_2, are also shown in figure 2b. Figure 2a, c and d show the simulated curves y(t) and z(t) as compared with the responding experimental data for temperatures 650, 725 and 750 °C respectively. It can be seen that there is a good agreement between the simulated and the experimental values. From the Arrhenius equation the activation energies for the perovskite formation is calculated to be 219 KJ/mol.

As an alternative, we can assume the starting film being fully pyrochlore (model B). We can also assume that the residual pyrochlore was uniformly distributed within the perovskite, i.e., the volume fraction of the residual pyrochlore is proportional to the volume of the perovskite. Now the transformation can be described as:

$$y \xrightarrow{k_2, n_2} z$$

we also assume

$y_r = c * z$

we have the following solutions:

$$y(t) = \frac{1}{1+c} \cdot \left(c + e^{-(1+c)k_2 t^{n2}}\right) \qquad (3)$$

$$z(t) = \frac{1}{1+c} \cdot \left(1 - e^{-(1+c)k_2 t^{n2}}\right) \qquad (4)$$

in the limit t →∞ these equations yield $y(\infty) = c/(1+c)$ and $z(\infty) = 1/(1+c)$, therefore c can be calculated from the amount of residual pyrochlore $r = c/(1+c)$. The parameters n_2, and k_2 can be obtained by minimising the sum of the squares of the errors (SSE) as defined before.

Figure 3a, b, c and d depict the simulated curves y(t) and z(t) (solid line and dotted-line respectively) according to equations (3) and (4) as compared with the responding experimental data (x and ◊ for pyrochlore and perovskite respectively) for temperatures 650, 700, 725 and 750 °C respectively. From Arrhenius plot the activation energy for the perovskite formation is 352 KJ/mol.

CONCLUSIONS

PST thin films for pyroelectric application have been deposited by rf sputtering and transformed into the desired perovskite structure by rapid thermal annealing. Two extreme cases where the starting material being either pure amorphous or pure pyrochlore have been studied in details. Equations have been derived and numerical calculation used to simulate the volume fractions for pyrochlore and perovskite as functions of annealing time. Transformation parameters k and n were obtained by comparing the simulated to the experimental intensities using a least-square curve fitting technique. Activation energies for phase transformations were calculated for both the extreme cases.

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Figure Legends:

Figure 1 XRD patterns for the PST thin films PST499, PST307 and PST183 which were deposited at 200, 300 and 450 ˚C respectively.

Figure 2 Experimental volume fractions (x and ◊ for pyrochlore and perovskite respectively) as functions of annealed time (seconds) as compared to the simulated (solid line for equation (1) the pyrochlore and dotted-line for equation (2) the pervoskite, respectively) curves from the model A for the PST thin films annealed at temperatures (a) 650 °C; (b) 700 °C; (c) 725 °C; and (d) 750 °C.

Figure 3 Experimental volume fractions (x and ◊ for pyrochlore and perovskite respectively) as functions of annealed time (seconds) as compared to the simulated (solid line for equation (3) the pyrochlore, and dotted-line for equation (4) the perovskite respectively) curves for the model B for the PST thin films annealed at temperatures (a) 650 °C; (b) 700 °C; (c) 725 °C; and (d) 750 °C.

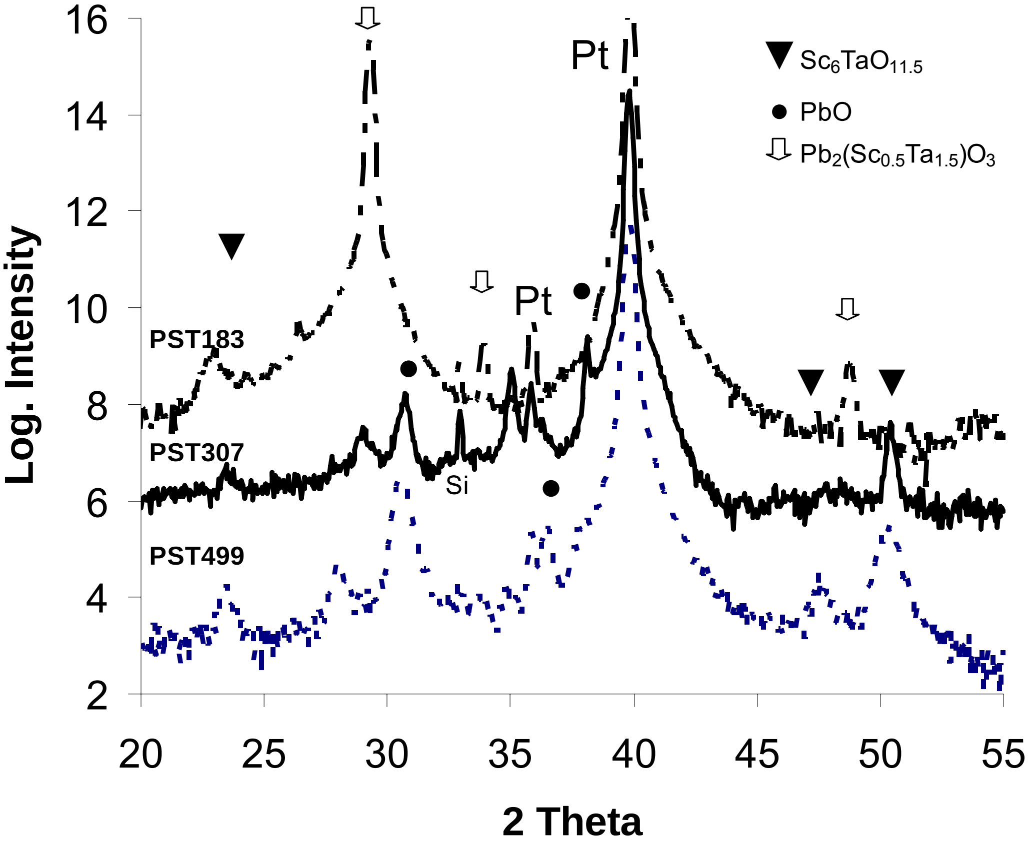
16
14
12
10
8
6
4
2
20
25
30
35
40
45
50
55
Log. Intensity
2 Theta
PST183
PST307
PST499
Pt
Pt
Si
▼ $Sc_6TaO_{11.5}$
● PbO
⇩ $Pb_2(Sc_{0.5}Ta_{1.5})O_3$

Figure 1

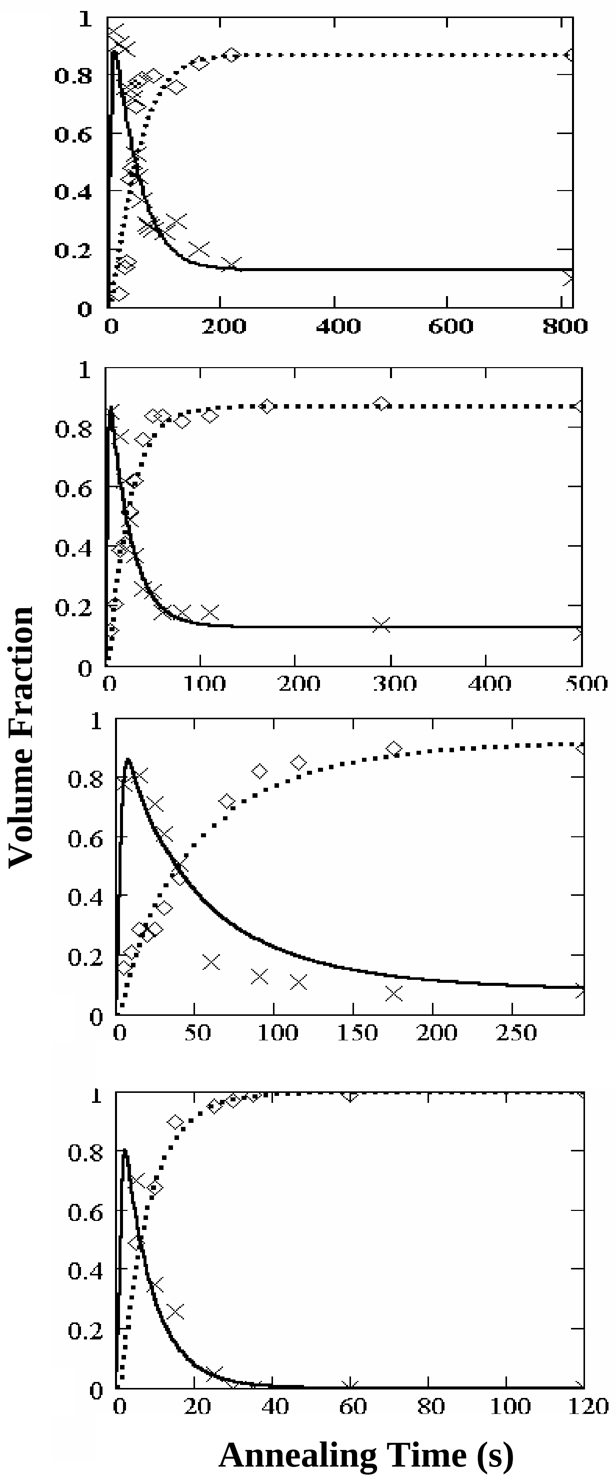
Volume Fraction
Annealing Time (s)
0
0.2
0.4
0.6
0.8
1
0
200
400
600
800
0
100
200
300
400
500
0
50
100
150
200
250
0
20
40
60
80
100
120

Figure 2

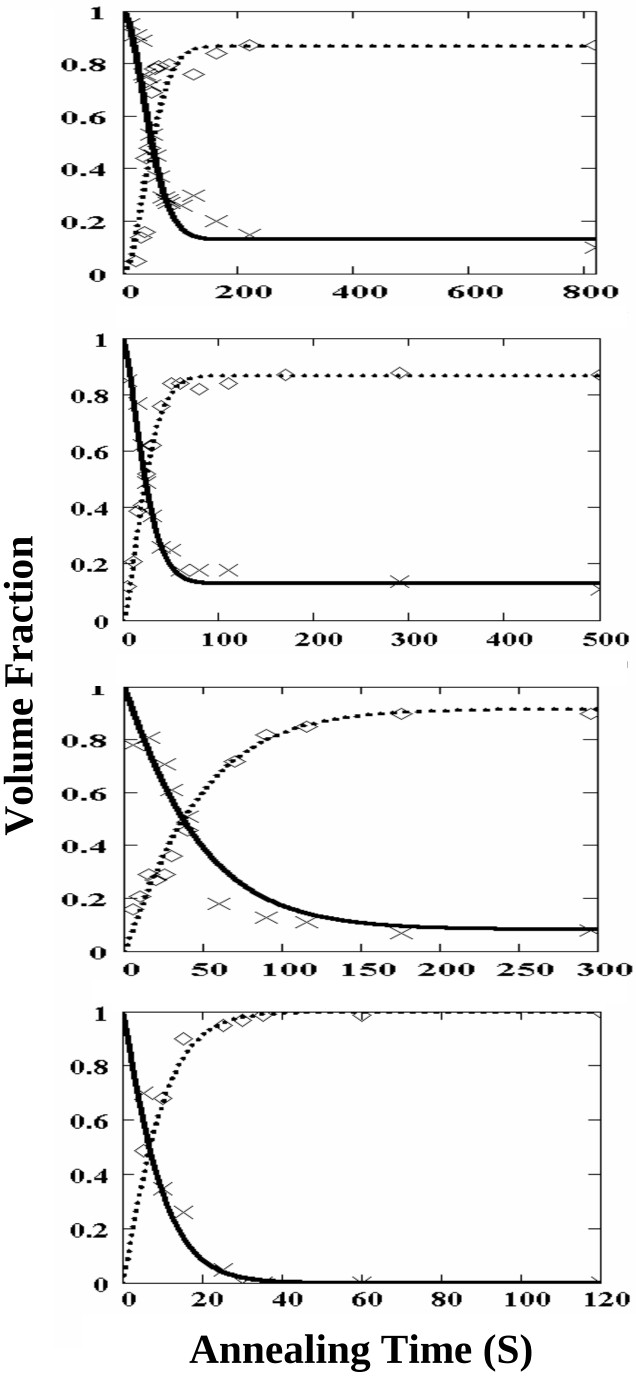
Volume Fraction
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
0
100
200
300
400
500
0
50
100
150
200
250
300
0
20
40
60
80
100
120
Annealing Time (S)

Figure 3