Annealing Induced Ordering of $SrTiO_3$ Thin Films Deposited by Laser Ablation Over Si Substrates

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Abstract

Strontium titanate thin films have been prepared at different oxygen pressures and with different post deposition annealing treatments. The films were deposited by laser ablation at room temperature on Si(001) substrates with a silica buffer layer. The as-deposited films are amorphous with smooth and uniform surface. As the annealing temperature increase they become more crystalline, presenting a cubic $SrTiO_3$ phase. The infrared characterization show that the silica layer also grows due to the annealing. The characteristics of this $SrTiO_3$ crystalline depend on the oxygen partial pressure. At low oxygen pressures the annealed films are polycrystalline. As the oxygen pressure increase the films become more textured so that at longer enough annealing times the films become (200) oriented. The results are discussed in terms of atomic diffusion in the films.

Keywords: $SrTiO_3$, Annealing, Infrared Spectroscopy, Modeling

Strontium titanate thin films have a wide range of applications, due to the high dielectric constant, low leakage current, low dielectric loss and good high frequency characteristics. From the application point of view optimized deposition conditions are essential, especially on semiconductor substrates due to the integration in current semiconductor technology [1].

In this work we present a study of strontium titanate thin films prepared at different oxygen pressures (pO_2) and with different post deposition annealing treatments. The films were deposited by pulsed laser ablation at room temperature on Si(001) substrates with a 45Å silica layer. The depositions were done with a KrF excimer laser (λ=248nm) at a fluence of 1.5J/cm^2. The annealings were performed in air at temperatures (T_{anneal}) 550ºC-750ºC during 15 to 90 min. The structural studies were performed by X-ray diffraction (XRD) with a Philips PW-1710 diffractometer using Cu Kα radiation. The surface was examined by scanning electron microscopy (SEM). Infrared reflectivity studies were performed on the films with a Bruker IFS 66V infrared spectrometer. The infrared spectra were modelled with thin film algorithms [2,3] to determine layer thickness and dielectric function parameters.

Figure 1 shows the SEM micrographs for films grown with $pO_2=1.8\times10^{-3}$mbar and $pO_2=2\times10^{-1}$mbar, as-deposited and after annealing at 750ºC. Figures 2a-b show the XRD spectra measured on these films. It is observed that the as-deposited films are amorphous with smooth and uniform surfaces. As the annealing temperature increases they become crystalline presenting a cubic $SrTiO_3$ phase. The grain sizes determined from the peak width are in the range 10-100 nm and increase with annealing temperature.

Figure 2c) shows the infrared spectra obtained on the samples deposited with $pO_2=2\times10^{-1}$mbar, before and after annealing for 60min. The main bands correspond to Ti-O stretching in $SrTiO_3$ [2] and Si-O stretching in silica [4]. The figure shows the progressive ordering of the strontium titanate layer so that for high T_{anneal} the reflectivity is described by the bulk parameters [2]. Also, the silica layer thickness grows from 45Å in the as deposited films to 70Å in the annealed ones. The total film thickness is in the range 90nm-130nm.

The characteristics of the $SrTiO_3$ crystalline phase vary with oxygen pressure. For low pO_2 the annealed films are polycrystalline presenting a structure similar to cubic bulk $SrTiO_3$ (a=3.905Å). A slight change to a (200) preferred orientation is observed for longer annealing times. The SEM micrographs show the formation of a grain-like surface for high T_{anneal}. As the oxygen pressure increases the films start to develop a (200) preferred orientation already for 15min annealing, and it tends to increase with annealing time (fig. 2b). The surface observed by SEM remains smooth in these films.

It is known that oxygen deficiency in $SrTiO_3$ leads to the formation of oxygen vacancies, mainly in the TiO_2 layers [5]. The high lattice mismatch between $SrTiO_3$ and silicon (a_{Si}=5.43Å), and the presence of oxygen vacancies lead to the disordered growth at room temperature observed in our films. However, annealing in air provide enough oxygen that migrate through the sample leading to the ordering of the $SrTiO_3$ layer and to the increase of the silica thickness. This effect is enhanced at higher annealing temperatures due to the increase of oxygen mobility.

On the other hand, lattice mismatch can be minimized if the face of the $SrTiO_3$ cube is on the Si(001) surface, but rotated relative to it. In fact, for a 45º angle the effective mismatch is (5.52-5.43)/5.43=1.7%, favoring a preferred (200) orientation. This texture process is expected to develop more rapid if the density of oxygen vacancies and disorder are lower, as in our films deposited with higher pO_2. However, the process is not complete in our samples due to the presence of the thin silica layer.

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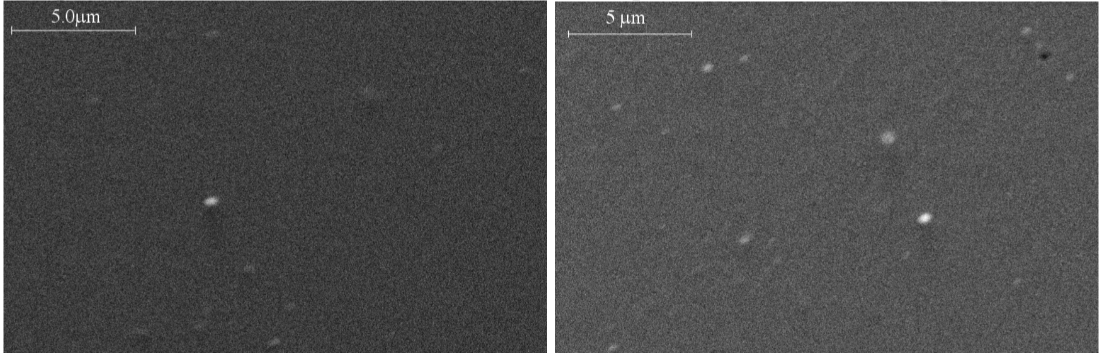
a) $pO_2=1.8\times10^{-3}$mbar; As deposited

c) $pO_2=1\times10^{-1}$mbar; As deposited



b) $pO_2=1.8\times10^{-3}$mbar; $T_{anneal}=750$ºC

d) $pO_2=1\times10^{-1}$mbar; $T_{anneal}=750$ºC

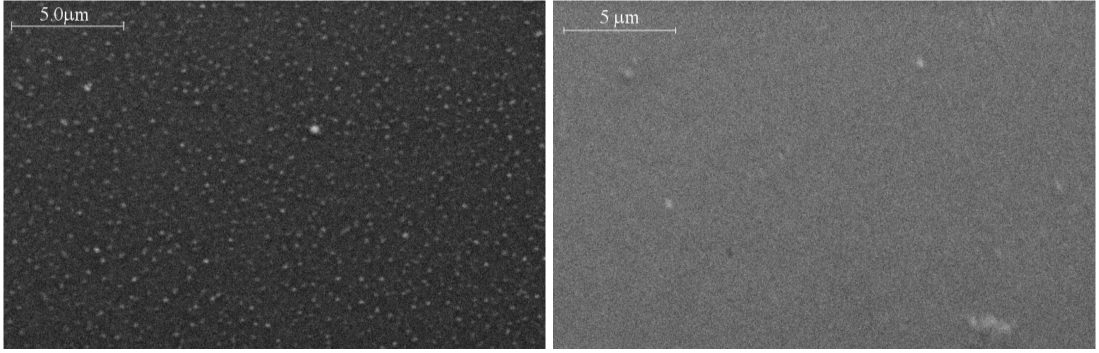


Figure 1

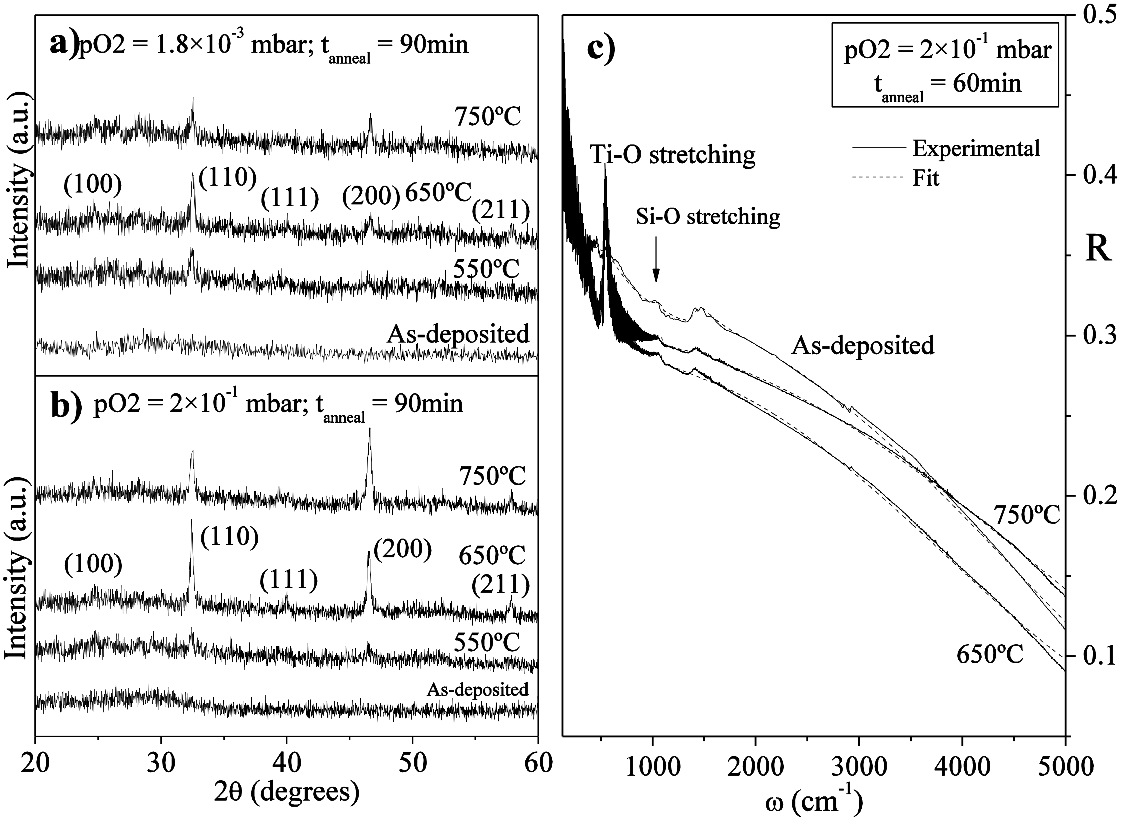

a) pO2 = 1.8×10^-3 mbar; t_anneal = 90min
750ºC
(100)
(110)
(111)
(200)
650ºC
(211)
550ºC
As-deposited
Intensity (a.u.)
b) pO2 = 2×10^-1 mbar; t_anneal = 90min
750ºC
(100)
(110)
(111)
(200)
650ºC
(211)
550ºC
As-deposited
Intensity (a.u.)
20
30
40
50
60
2θ (degrees)
c)
pO2 = 2×10^-1 mbar
t_anneal = 60min
Ti-O stretching
Si-O stretching
Experimental
Fit
As-deposited
750ºC
650ºC
R
0.5
0.4
0.3
0.2
0.1
1000
2000
3000
4000
5000
ω (cm^-1)

Figure 2