INFRARED CHARACTERIZATION OF STRONTIUM TITANATE THIN FILMS

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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. Infrared reflectance measurements were performed in order to determine relevant film parameters such as layer thicknesses and chemical composition. The infrared reflectance spectra were modeled with thin film algorithms and these were fitted to the experimental spectra. The model included the strontium titanate film and a silica buffer layer represented by a set of damped harmonic oscillators, and the silicon substrate represented by a Drude term for free carriers. The fitting procedure provided the extraction of the dielectric functions of the layers and the substrate using only the reflectance spectrum. The as-deposited films are found to be amorphous with smooth and uniform surface. Their infrared spectra present peaks corresponding to modes with high damping constants. The results show that by increasing the annealing temperature and time the strontium titanate layer becomes more ordered so that it can be described by its $SrTiO_3$ bulk mode parameters. Also, the silica layer grows along with the ordering of the strontium titanate film, due to oxidation during annealing.

KEYWORDS: Strontium Titanate, Infrared Spectroscopy, Modeling.

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Strontium titanate thin films have a wide range of applications, due to 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]. Infrared spectroscopy provides excellent sensitivity to layer composition, including chemical bond densities (through their vibrational mode intensities), and free carriers, with enhanced immunity to roughness induced scattering. Also, it is as a non-destructive characterization technique making it suitable to control film deposition and processing parameters.

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 objective is to apply the infrared technique to determine relevant film parameters such as layer thicknesses and chemical composition. 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}) 550°C-750°C 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 reflectivity measurements were done at normal incidence in the spectral range 100-5000 cm^{-1}.

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 750°C. Figures 2 shows 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.

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. The surface observed by SEM remains smooth in these films.

The infrared spectra were modelled with thin film algorithms to determine layer thicknesses, index of refraction and extinction coefficients, and other dielectric function parameters. The model took into account the three relevant layers corresponding to the strontium titanate film, the silica buffer layer and the substrate.

The dielectric function of the strontium titanate layer was modelled by the factorised form [2]:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_j \frac{\Omega_{LOj}^2 - \omega^2 + i\gamma_{LOj}\omega}{\Omega_{TOj}^2 - \omega^2 + i\gamma_{TOj}\omega}$$

where Ω_{TOj}, Ω_{LOj} are the transversal and longitudinal frequencies of the j^{th} mode and γ_{TO}, γ_{LO} are the corresponding damping constants. The factorised form of the dielectric function is more suitable than the classical oscillator form, for ionic crystals having strong infrared bands with large TO-LO splittings, as is the case of strontium titanate. The silica layer dielectric function was modelled using its bulk values taken from [3].

Pure silicon has a dielectric function ($\varepsilon(\omega)=3.4$) that is approximately constant in the measured frequency range [4]. Also its extinction coefficient is vanishing small in this range so that the dielectric function is real. However, the silicon substrates that were used were doped and presented a p-character (conduction by holes). Thus, its dielectric function must take into account the presence of free charges and this was done by using a plasmon term. So, the substrate dielectric function was written as:

$$\varepsilon(\omega) = \varepsilon_{\infty p} - \frac{\omega_p^2}{\omega^2 + i\gamma_p \omega}$$

where $\omega_p^2 = 4\pi Ne^2/m^*$ defines the bulk plasma frequency due to free carriers of density N and effective mass m*, and γ_p is the free-carrier damping constant. The mobility μ can be calculated from the damping constant, through $\mu = e/m^*\gamma$. For our substrates we used $m^* = 0.37m_e$, where m_e is the electron mass. We express all the frequencies in wave numbers (cm^{-1}), i.e. $\omega(cm^{-1}) = \omega(\text{in rad/s})/2\pi c$.

Using these expressions the dielectric function of each layer was calculated and the corresponding complex refraction index $\tilde{N}$ was obtained by using the relation $\tilde{N}_{layer} = n_{layer} - ik_{layer} = \sqrt{\varepsilon_{layer}}$ (n being the refraction index and k the extinction coefficient). From the complex refraction indexes, the reflectivity of this two layer system on a substrate was determined using the Fresnel equations [3]. The fitting algorithm iteratively varied the parameters until the weighted mean square difference was minimized between the measured and simulated reflectivity spectra.

From the fittings to the experimental curves it was possible to obtain, for each film, the silica and strontium titanate layer thicknesses, and the substrate carrier concentration and mobility. Also, the strontium titanate Ω_{TOj}, Ω_{LOj}, γ_{TOj} and γ_{LOj} mode parameters were determined from the fittings, and they were particularly important to understand the chemical

evolution of the films. In our samples we observed that reflectivity could be well described using the bulk strontium titanate Ω_{TOj}, Ω_{LOj} mode frequencies, but the corresponding damping constants were very sensitive to the layer ordering.

Figure 3 shows the infrared spectra obtained on the samples deposited with $pO_2=1.8\times10^{-3}$mbar, $pO_2=2\times10^{-2}$mbar and $pO_2=2\times10^{-1}$mbar, after annealing for 30min. The main bands correspond to Ti-O stretching in $SrTiO_3$ [5] and Si-O stretching in silica [6]. The strontium titanate layer thickness determined from the fittings was is in the range 80nm-130nm and remained practically constant for the annealed films. The obtained substrate carrier concentration and mobility were $1\times10^{18}cm^{-3}$ and $20cm^2/Vs$ and also remained approximately constant during the annealing.

Figures 4a-b show the γ_{TO} and γ_{LO} damping constants obtained from the fittings to the measured infrared reflectivity. The figures show the progressive ordering of the strontium titanate layer so that for high T_{anneal} the reflectivity is described by the bulk γ_{TO} and γ_{LO} parameters [5]. Also, the silica layer thickness grows from 45Å in the as deposited films to as much as 70Å in the annealed ones (fig. 4c). This effect is higher in the samples deposited with low pO_2 due a stronger oxygen deficiency throughout the films.

It is known that oxygen deficiency in $SrTiO_3$ leads to the formation of oxygen vacancies, mainly in the TiO_2 layers [7]. The high lattice mismatch between $SrTiO_3$ (a=3.905Å) and silicon (a_{Si}=5.43Å), and the presence of oxygen vacancies lead to the disordered growth at room temperature observed in our films. This in turn originates high strontium titanate γ_{TO} and γ_{LO} damping constants, as observed in the infrared results. 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. The corresponding $SrTiO_3$ γ_{TO} and γ_{LO} damping

parameters then decrease towards the bulk values, as observed. This effect is enhanced at higher annealing temperatures due to the increase of oxygen mobility.

With the infrared modeling procedure here described we were able to extract important thin film physical parameters using only the reflectance spectrum, which makes this technique suitable to control film deposition and processing.

References

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Figure Captions

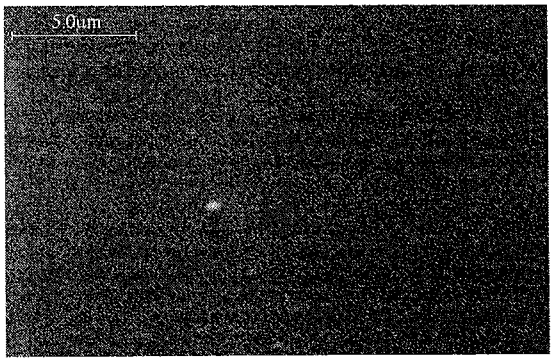
Figure 1: SEM micrographs for films grown with a)-b) $pO_2=1.8\times10^{-3}$mbar and c)-d) $pO_2=2\times10^{-1}$mbar, as-deposited and after annealing at 750°C

Figure 2: X-ray diffraction spectra for films grown with a)-b) $pO_2=1.8\times10^{-3}$mbar and c)-d) $pO_2=2\times10^{-1}$mbar, after annealing for 15min and 90 min.

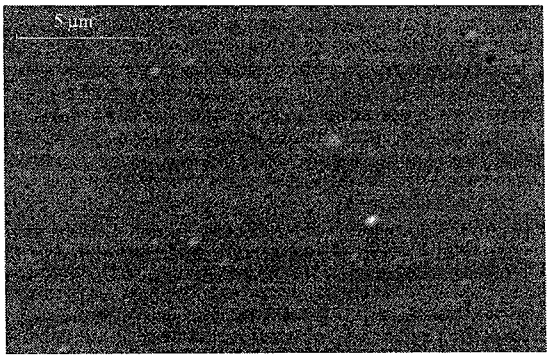
Figure 3: Infrared reflectance spectra for films grown with a) $pO_2=1.8\times10^{-3}$mbar, b) $pO_2=2\times10^{-2}$mbar and c) $pO_2=2\times10^{-1}$mbar, after 15 min annealing. Also shown are the corresponding fitting curves.

Figure 4: TO a) and LO b) damping constants obtained from the fitting to the measured infrared reflectivity. In c) is shown the silica layer thickness obtained from these fits.

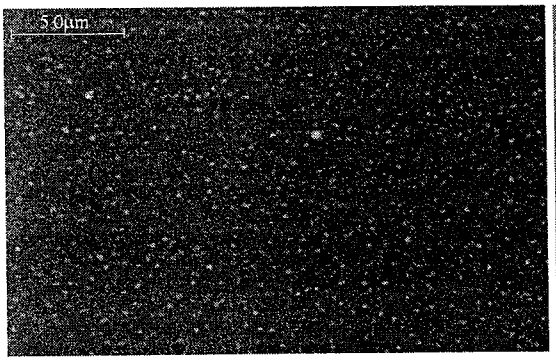
a) $pO_2=1.8\times10^{-3}$mbar; As deposited



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



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



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

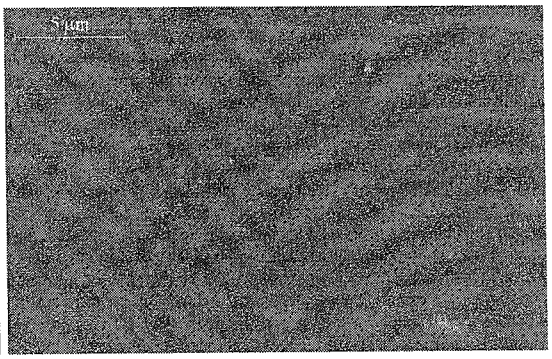


Figure 1

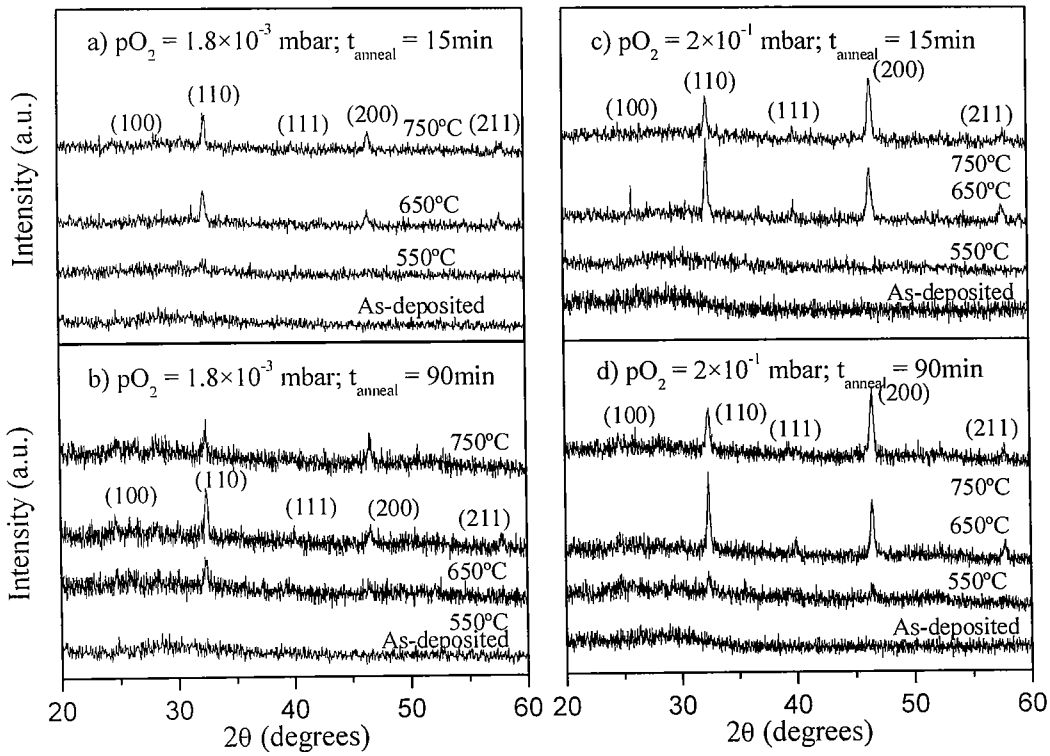

a) $pO_2 = 1.8\times10^{-3}$ mbar; t_{anneal} = 15min
(100)
(110)
(111)
(200)
(211)
750°C
650°C
550°C
As-deposited
b) $pO_2 = 1.8\times10^{-3}$ mbar; t_{anneal} = 90min
c) $pO_2 = 2\times10^{-1}$ mbar; t_{anneal} = 15min
d) $pO_2 = 2\times10^{-1}$ mbar; t_{anneal} = 90min
Intensity (a.u.)
2θ (degrees)
20
30
40
50
60

Figure 2

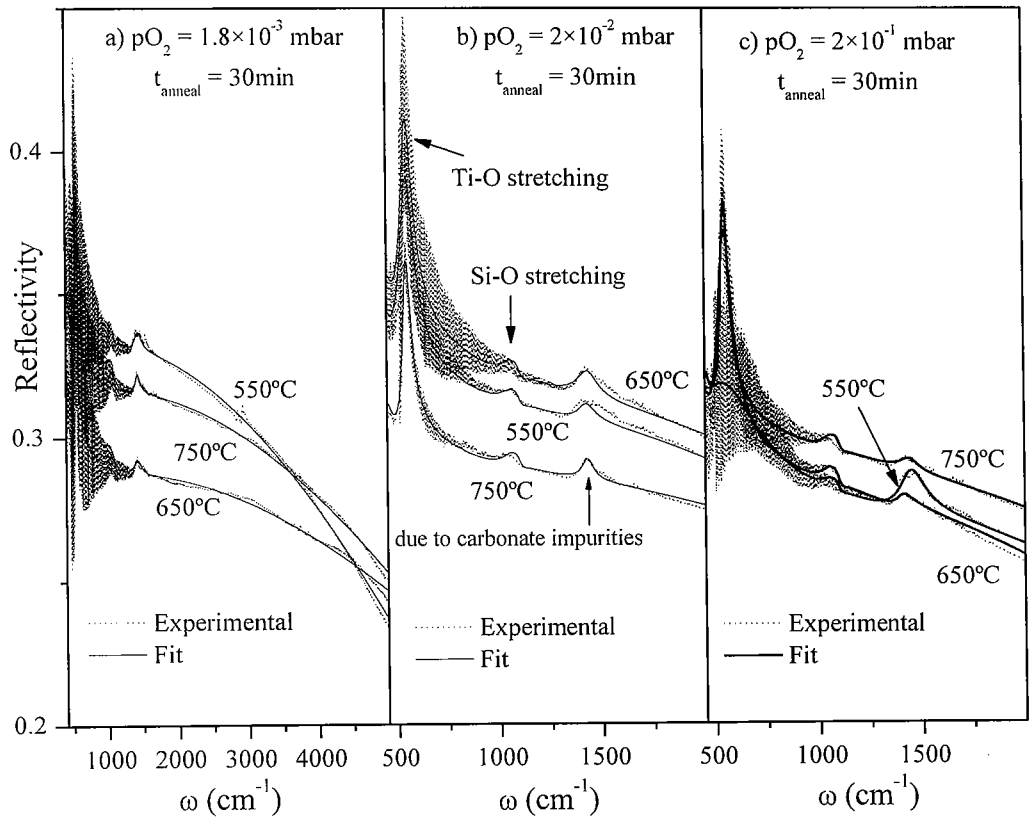

a) pO2 = 1.8×10-3 mbar
tanneal = 30min
b) pO2 = 2×10-2 mbar
tanneal = 30min
c) pO2 = 2×10-1 mbar
tanneal = 30min
Reflectivity
0.4
0.3
0.2
Ti-O stretching
Si-O stretching
550°C
750°C
650°C
650°C
550°C
750°C
550°C
750°C
650°C
due to carbonate impurities
Experimental
Fit
Experimental
Fit
Experimental
Fit
1000 2000 3000 4000
500 1000 1500
500 1000 1500
ω (cm-1)
ω (cm-1)
ω (cm-1)

Figure 3

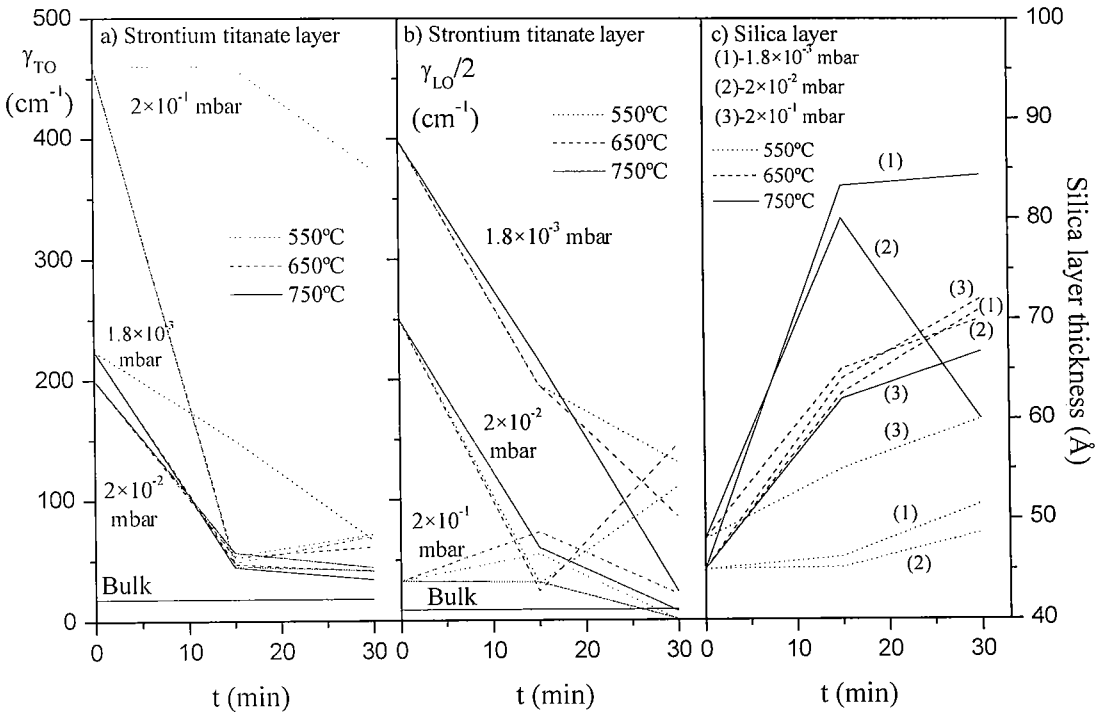

a) Strontium titanate layer
γ_{TO} (cm^{-1})
2×10^{-1} mbar
550°C
650°C
750°C
1.8×10^{-3} mbar
2×10^{-2} mbar
Bulk
t (min)
b) Strontium titanate layer
γ_{LO}/2 (cm^{-1})
550°C
650°C
750°C
1.8×10^{-3} mbar
2×10^{-2} mbar
2×10^{-1} mbar
Bulk
t (min)
c) Silica layer
(1)-1.8×10^{-3} mbar
(2)-2×10^{-2} mbar
(3)-2×10^{-1} mbar
550°C
650°C
750°C
Silica layer thickness (Å)
t (min)

Figure 4