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Fourier transform–infrared and optical studies on sol–gel synthesized $SrTiO_3$ precursor films

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$SrTiO_3$ precursor thin films were deposited on KBr single crystals and fused silica substrates by the sol–gel technique. Fourier transform–infrared (FT–IR) spectra, ultraviolet–visible spectra and X-ray diffraction spectra were recorded after the samples were cured at various temperatures. FT–IR spectra showed a gradual decrease in –OH concentration indicating removal of hydroxyls and reduction in peaks belonging to organic groups indicating the removal of organics. After annealing at 500 °C, the peak due to $SrTiO_3$ crystallites ($\sim 500\ \mathrm{cm}^{-1}$) began to appear, indicating crystallization. The optical spectra showed an increase in refractive index due to densification as the curing temperature increased. With increase in curing temperature, the thickness of the film decreased, indicating densification due to pore collapse. The optical band gap also changed with annealing due to the structural transformation from amorphous to crystalline phase. X-ray diffraction spectroscopy confirmed the structural changes.

1. Introduction

The sol–gel process has been identified as a major material processing technology in recent years owing to its versatility in synthesizing new materials for a variety of applications. Fabrication of ceramic oxide thin films by the sol–gel process has become an important activity in the area of thin-film technology, owing to its ease of fabrication, better reproducibility, cost effectiveness and purity of the end products. The structural and physical properties of the thin films produced by the sol–gel process strongly depends on the selection of starting material [1], the rate of hydrolysis and condensation, the chemical modifications of the sol–gel system and other processing parameters [2]. In fact, these parameters can be precisely controlled to tailor the properties of the sol–gel-derived thin films. The change in various physical properties of the precursor thin films made by the sol–gel process during heat treatment can be correlated with the structural and microstructural changes occurring in the film during consolidation [3, 4]. In this regard it is interesting to study the structural and microstructural evolution in sol–gel-processed ceramic thin films. In this paper we report structural and microstructural evolution in sol–gel-derived $SrTiO_3$ precursor films with heat treatment.

Strontium titanate ceramics and thin films were reported earlier by many researchers using the sol–gel process with different starting materials [5–8]. In present work, we used strontium 2-ethyl hexanoate as the strontium source and titanium isopropoxide as the titanium source. Ethyl alcohol was used as the solvent. Acetyl acetone was used as a chelating agent to obtain better quality films. The thin films made from the above precursor were studied using Fourier transform–infrared (FT–IR), ultraviolet–visible (UV–VIS) spectroscopy and X-ray diffraction (XRD) techniques.

2. Experimental procedure

The precursor system used in the preparation of $SrTiO_3$ thin film was titanium isopropoxide and strontium 2-ethyl hexanoate. Strontium 2-ethyl hexanoate (3.74 g) was dissolved in 25 ml ethanol and 1 ml acetyl acetone to give a pale yellow solution. To this mixture 0.18 ml water was added for hydrolysis. Titanium isopropoxide was then added to the above solution, dropwise, under constant stirring. The solution was then refluxed at 80 °C for 1 h, cooled to room temperature and then filtered. The sol thus obtained was spin coated on to KBr crystals, fused silica substrates and single-crystal silicon wafers (1 0 0). The substrates were then cured at 300 °C for 10 min to remove the solvent. Multiple coatings of the sol were done on the substrates to increase the thickness of the deposited films.

The films deposited on KBr single crystals were used for FT–IR spectroscopy studies. FT–IR spectra were recorded on these samples using a Nicolet spectrophotometer. The UV–VIS transmission spectra of the samples made on fused silica substrates were done using a Shimadzu 160A spectrophotometer. X-ray diffraction was performed on the samples deposited on single-crystal silicon wafers (1 0 0) using a Siemens 500 D diffractometer with CuK_α X-ray radiation.

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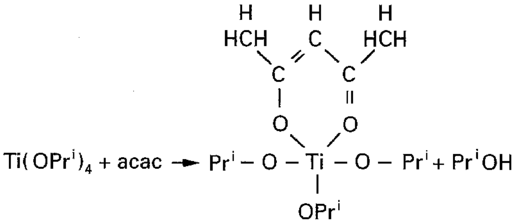
3. Results and discussion

3.1. FT–IR studies

The FT–IR spectra of $SrTiO_3$ precursor films were recorded after the films had been cured at temperatures of 30, 150, 250, 350, 450, 550 and 650 °C. Because titanium isopropoxide is complexed with acetyl acetone and water, the precursor solution must have undergone partial hydrolysis of the alkoxide and possible cross reactions, giving rise to a complex FT–IR spectrum. In order to resolve this spectrum, different components of the precursor solution were examined separately. Fig. 1a shows the FT–IR spectrum of titanium isopropoxide chelated using acetyl acetone (1:1 molar ratio). The absorption band of 620 cm^{-1} is due to titanium isopropoxide and bands at 1590 and 1550 cm^{-1} are due to acac groups bonded to titanium [9]. This bonding increases the coordination of titanium from 4 to 5 as indicated in Equation 1



$$Ti(OPr^i)_4 + acac \rightarrow Pr^i-O-Ti(acac)(OPr^i)-O-Pr^i + Pr^iOH$$

(1)

Fig. 1b shows the FT–IR spectrum of strontium ethyl hexanoate, which exhibits strong absorption bands in the 1300–1600 cm^{-1} region due to symmetric and asymmetric stretching vibration of the carboxylate groups. Fig. 1c is the FT–IR spectrum of strontium ethyl hexanoate precursor cured at 400 °C, which shows a peak at 1430 cm^{-1} indicating the pyrolysis and subsequent transformation of strontium ethyl hexanoate into strontium carbonate.

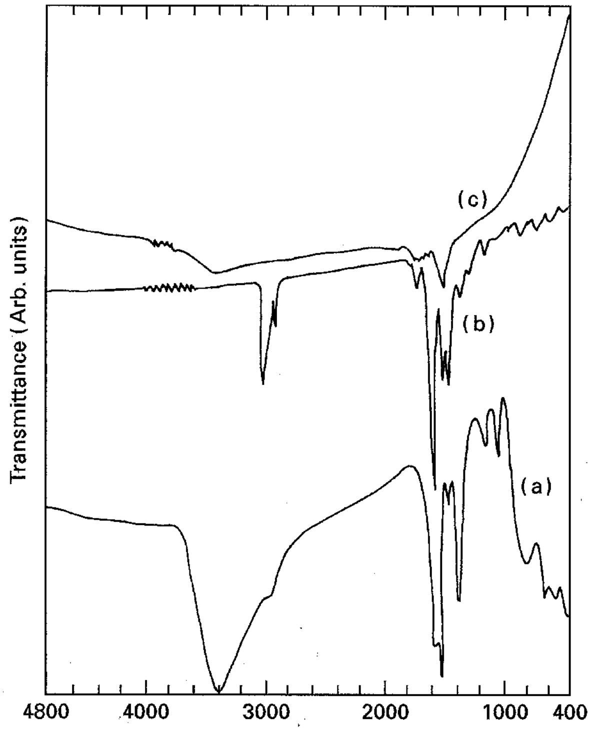


Figure 1 FT–IR spectra of (a) titanium isopropoxide chelated using 1 mol acetyl acetone, (b) strontium ethyl hexanoate dissolved in methanol and deposited on KBr at room temperature, and (c) strontium ethyl hexanoate thin film cured at 400 °C.

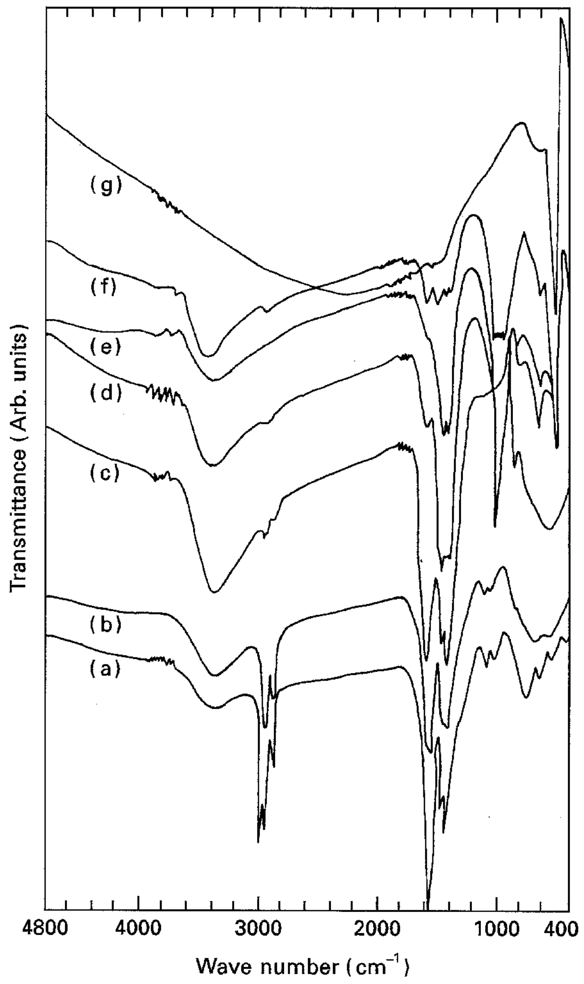


Figure 2 FT–IR spectra of $SrTiO_3$ precursor films annealed at different temperatures. (a–g) Films annealed at 30, 150, 250, ,350, 450, 550 and 650 °C, respectively.

Fig. 2a–g show the FT–IR spectra of $SrTiO_3$ precursor films fired at 30, 150, 250, 350, 450, 550 and 650 °C, respectively. The absorption band seen around 3400 cm^{-1} in Fig. 2a, which is progressively decreasing in intensity as the curing temperature is increased (see Fig. 2f), is due to the hydrolysis of titanium isopropoxide. The decrease in its intensity can be attributed to the condensation reaction and subsequent loss of water due to evaporation. The exact nature of these hydroxyls cannot be judged as they are not resolved in the spectra. The absorption bands at 2800–3000 cm^{-1} are due to CH stretching. Here also, the bands show a decrease in intensity after curing at elevated temperatures. These bands are absent in spectra of films cured above 450 °C, showing removal of organics.

A comparison of the band in the region of 1400–1600 cm^{-1} with that of pure strontium ethyl hexanoate and titanium isopropoxide, shows that most of these bands are due to organics belonging to the constituents. The bands at 1590 and 1530 cm^{-1}, which are due to the formation of titanium isopropoxide–acac complex, is almost masked by the strong carboxylate bands. The intensity of these bands also decreases and vanishes above a curing temperature of 450 °C showing the removal of organics. The bands at 2335–2350 cm^{-1} are due to CO_2 absorbed on the film which has evolved from the pyrolysis of organic contents of the film. As pyrolysis of the film continues, it is seen that a new band appears at 1015 cm^{-1}, which may be due to the formation of some new bonds in the film. A comparison of the spectra of strontium ethyl hexanoate cured at 400 °C under similar conditions (Fig. 1c) shows that this band is not due to strontium compounds. A thin film of titanium isopropoxide–acac complex hydrolysed and cured at 400 °C, also does not show this peak. This means the new band may be due to a reaction between strontium oxide and titanium oxide.

The low-frequency region of the spectrum shows a mixture of bands due to the carboxylate group and alkoxides. The formation of a new band around 450 cm^{-1} for samples cured above 500 °C is due to crystallization of strontium titanate [10].

3.2. Optical properties

Optical properties of $SrTiO_3$ thin films were studied from the optical transmission spectra recorded in the wavelength range 200–1100 nm. The films used in this study were deposited on 1 mm thick fused silica substrates. Calculation of the refractive index and thickness of the films was done using the method applied by Manifacier *et al.* [11].

Fig. 3 shows the variation of thickness of $SrTiO_3$ precursor film with annealing temperature. The films show sharp shrinkage in the range 300–450 °C (about 35%). This shrinkage may be due to the attractive forces provided by the bond formation during the condensation reaction. The increase in pore volume created by the removal of organics may weaken the gel structure resulting in the collapse of the gel network, leading to shrinkage of the film. Above 450 °C, the reduction in thickness is low and is attributed to structural relaxation.

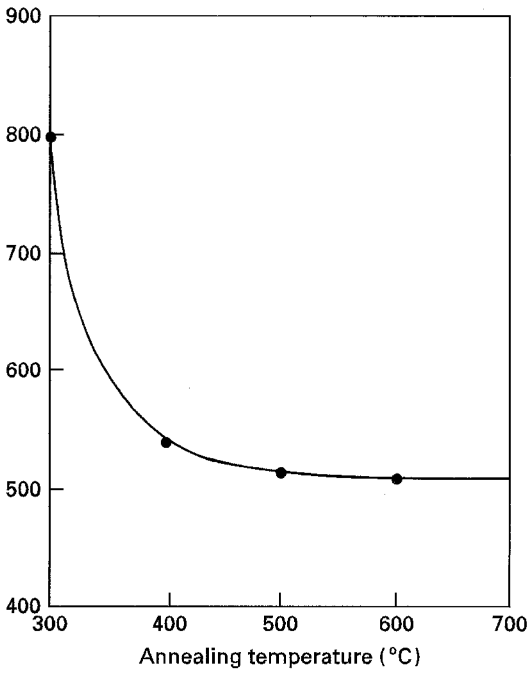


Figure 3 Thickness variation of $SrTiO_3$ precursor film with curing temperature.

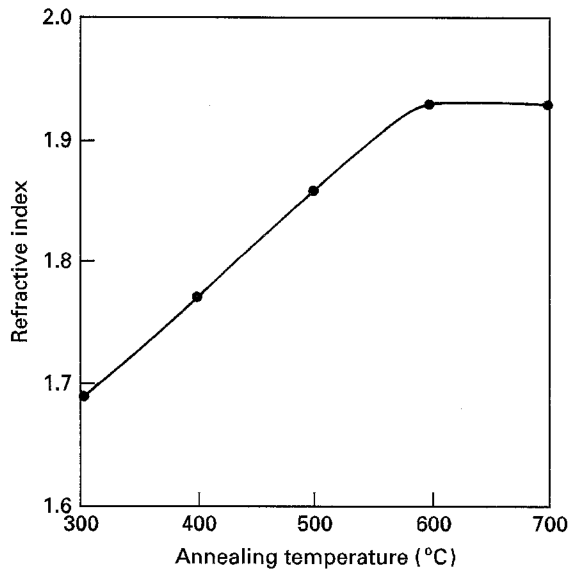


Figure 4 Variation of refractive index of $SrTiO_3$ precursor films with curing temperature.

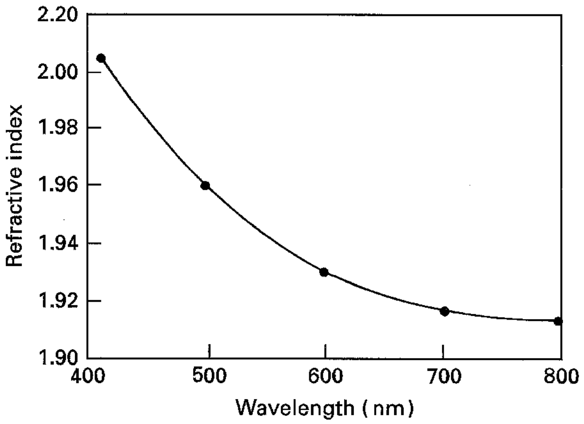


Figure 5 Wavelength dispersion of $SrTiO_3$ thin films deposited on fused silica and annealed at 600 °C.

The variation of refractive index with annealing is represented in Fig. 4. At 300 °C the films have a refractive index of 1.69. This increases with curing temperature and attains a constant value of 1.93 around 600 °C; this indicates the maximum densification of the films.

Fig. 5 shows the wavelength dispersion curve of $SrTiO_3$ thin films. The dispersion curve is fairly flat above 600 nm and rises rapidly towards the shorter wavelength region, showing the typical shape of a dispersion curve near an electronic interband transition [12]. According to the single electronic oscillator model suggested by DiDomenico and Wemple [13], the index of refraction is given by

$$n^2 - 1 = \frac{S_0\lambda_0^2}{1 - (\lambda_0/\lambda)^2} \qquad (2)$$

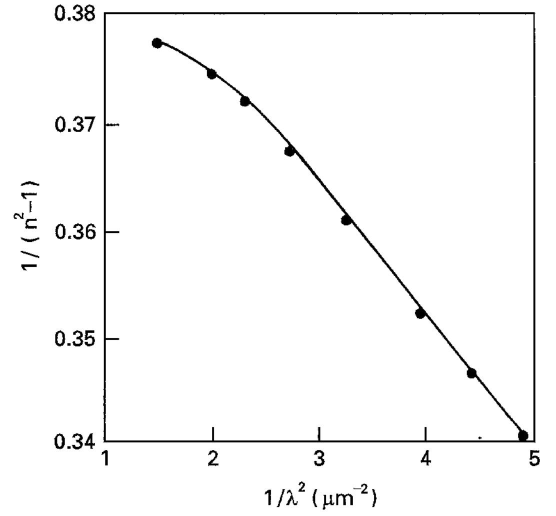


Figure 6 Variation of refractive index of $1/(n^2 - 1)$ as a function of $1/\lambda^2$.

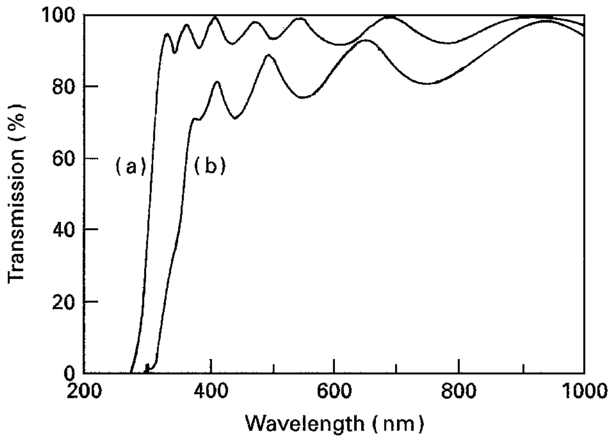


Figure 7 The optical transmission spectra of (a) amorphous and (b) polycrystalline $SrTiO_3$ thin films on fused silica.

where λ_0 is the average oscillator position and S_0 is an average oscillator strength. In Fig. 6, the quantity $1/(n^2 - 1)$ is plotted against $1/\lambda^2$. The curve is a straight line showing the validity of the above model.

Fig. 7 shows the transmission spectra of $SrTiO_3$ thin films annealed at 400 and 550 °C. The film annealed at 400 °C was amorphous, having a band gap of about 3.8 eV. The band gap for the film annealed at 550 °C was about 3.4 eV, which is near the single-crystal value reported [14]. The change in band gap from 3.8 eV to 3.4 eV suggests the occurrence of crystallinity in the film annealed above 550 °C. This fact was supported by XRD and FT–IR studies.

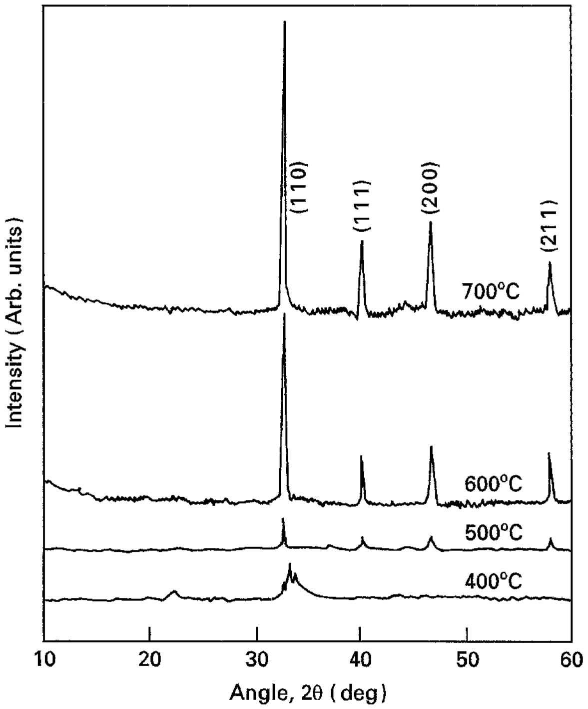


Figure 8 XRD spectra of $SrTiO_3$ thin films annealed at different temperatures.

3.3. X-ray diffraction studies

Fig. 8a–d show the XRD spectra of $SrTiO_3$ films deposited on silicon (1 0 0) substrates and annealed at 400, 500, 600 and 700 °C, respectively. The spectrum of the sample annealed at 400 °C was found to be amorphous. At 500 °C, the film begins to crystallize, as indicated by the emergence of characteristic peaks of $SrTiO_3$. XRD spectra of samples annealed at 600 and 700 °C show well-defined diffraction peaks, indicating that the films are crystallized. Lattice parameters calculated from the *d* values of the peaks in the spectrum are $a = b = c = 0.390$ nm, which was in agreement the ASTM values (data card 5–634).

The XRD spectra shows the onset of crystallization around an annealing temperature of 500 °C. It is interesting to note that change in the optical absorption edge in the UV–VIS spectra as well as the appearance of a new band at 450 cm^{-1} in the FT–IR spectra appear in the sample around an annealing temperature of 500 °C.

4. Conclusion

$SrTiO_3$ precursor films have been grown on fused silica, single-crystal KBr and silicon wafers (1 0 0) using the sol–gel technique. The transformation of these films from the initial inorganic polymer state to amorphous and then to polycrystalline $SrTiO_3$ ceramic thin films, was studied using FT–IR, UV–VIS and XRD spectroscopy techniques. The results obtained from various observations conducted in the present study could be correlated.

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