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High dielectric constant of $SrTiO_3$ thin films prepared by chemical process

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$SrTiO_3$ thin films were prepared by the polymeric precursor method and deposited by spin-coating onto Pt/Ti/SiO_2/Si(100) substrates. The spin-coated films heat treated at 700°C were crack-free, dense, and homogeneous. Microstructural and morphological evaluations were followed by grazing incident X-ray, scanning electron microscopy and atomic force microscopy. Dielectric studies indicated a dielectric constant of about 475, which is higher than that of ceramic $SrTiO_3$, and a factor dissipation of about 0.050 at 100 kHz. $SrTiO_3$ thin films were found to have paraelectric properties with *C-V* characteristics. © *2000 Kluwer Academic Publishers*

1. Introduction

Ferroelectric thin films have lately been investigated for application in integrated memory devices. To increase the integration density of dynamic random access memories (DRAM's) [1–3], high dielectric constant materials are required to obtain large charge storage density. Ferroelectric properties such as polarization hysteresis are not essential for DRAM applications, which require only a high dielectric constant with good insulating properties.

In the last few years, perovskite oxides such as strontium titanate ($SrTiO_3$) [4–6] have been intensively researched due to their structural and dielectric features. $SrTiO_3$ is a well-known perovskite-structured material with a cubic paraelectric phase above 105 K and a bulk dielectric constant of about 300 for sintered ceramics [7].

Several techniques have been used to produce $SrTiO_3$ thin films, i.e., sputtering [8, 9], sol-gel [10], laser ablation [11,12], MOCVD [13], etc. However, very few reports are available on the preparation of $SrTiO_3$ thin films by the polymeric precursor method (known as "Pechini's method") [14–17]. One of the few reports is by Zanetti *et al*. [18], who prepared $SrTiO_3$ thin film by the Pechini method, producing films that were generally crack-free and homogenous, although no detailed electrical characterization was reported. In this work, we report on the production of crack-free, dense, homogeneous thin films such as strontium titanate, as well as on the electrical properties, using the Pechini method.

2. Experimental procedure

Fig. 1 shows the flow chart of $SrTiO_3$ synthesis used in this study, while Table I lists the raw materials and sources used for $SrTiO_3$ synthesis. Titanium citrates were formed by the dissolution of titanium isopropoxide in a water solution of citric acid (60°–70° C). After homogenization of the Ti solution, $SrCO_3$ was slowly added and, after complete dissolution of the $SrCO_3$ salt, ethylene glycol was added to promote polymerization of the mixed citrates by polyesterification reaction. The molar ratio among the strontium and titanium cations was 1 : 1, the citric acid/metal ratio was fixed at 1.00, and the citric acid/ethylene glycol ratio was defined as 60/40 (mass ratio).

Pt/Ti/SiO_2/Si(100) wafers were used as substrates. The substrate was spin-coated by dropping a small amount of the polymeric precursor solution onto it. Rotation speed and spin time were fixed, respectively, at 4500 rpm and 30 s. After deposition, each layer was dried on a hot plate at 150°C for 20 min to remove residual solvents.

The heat treatment was carried out in two stages: initial heating at 400°C for 2 h at a heating rate of 5°C/min to pyrolyze the organic materials, followed soon thereafter by heating at 700°C during 2 h to crystallize them. Film thickness was controlled by adjusting the number of coats and each layer was pyrolyzed at 400°C and crystallized at 700°C before the next layer was coated. Five layers were used in this study.

The $SrTiO_3$ films were structurally characterized using X-ray diffraction (XRD) (Cu K_α radiation), and the diffraction patterns recorded on a Siemens D5000 machine in an θ–2θ configuration, using a graphite monochromator. Microstructural characterization was performed by scanning electron microscopy (SEM) (Zeiss, DSM940A). The film thickness was measured by a thin film cross-section analysis made by SEM. Atomic force microscopy (AFM) was used to obtain a

TABLE I Raw materials used in the $SrTiO_3$ synthesis

Material	Source	Purity
Titanium isopropoxide ($Ti(OCH(CH_3)_2]_4$)	Aldrich Chemical	99.9%
Strontium Carbonate ($SrCO_3$)	Riedel de Haen A. G.	99.99%
Ethylene glycol (CH_2OHCH_2OH)	E. Merck	99.9%
Citric acid ($C_6H_8O_7{\cdot}H_2O$)	E. Merck	99.9%

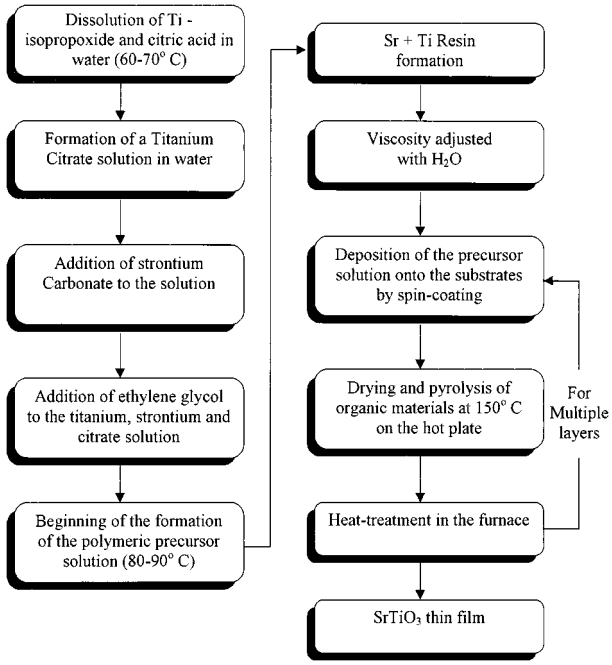

Figure 1 Flow-chart illustrating the procedure for the preparation of $SrTiO_3$ solution and film production.

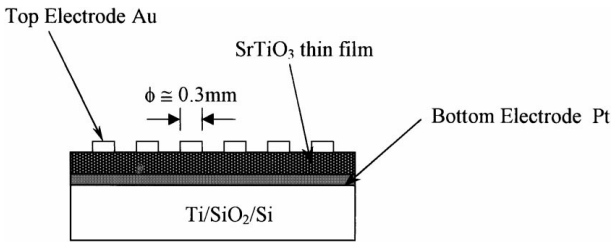

Figure 2 Metal-insulator-metal (MIM) configuration used in this study.

3D image reconstruction of the sample surface. These images allow for an accurate analysis of the sample surface and the quantification of very important parameters such as roughness and grain size. A Digital Instruments Multi-Mode Nanoscope IIIa was used.

To carry out the electrical measurements, 0.3 mm diameter Au electrodes were deposited by sputtering through a designed mask onto the film surfaces (area of 1cm $\times$ 1cm) to form metal-insulator-metal capacitors (MIM). A schematic view of the capacitor structure is shown in Fig. 2. The dielectric properties were measured as a function of frequency using a Hewlett-Packard (4194A) impedance/gain phase analyzer.

The capacitance-voltage characteristic was measured for MIM configuration using a small AC signal of 10 mV at 100 kHz. The signal was applied across the sample, while the DC electric field was swept from positive bias to negative bias and back again to positive bias (C-V curves). Dielectric constant and dissipation factor values were measured in a frequency range of 100 Hz–10 MHz in 600-nm-thick films. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Crystallographic structure

The crystallographic structure of the films was examined using the X-ray-diffraction technique (XRD).

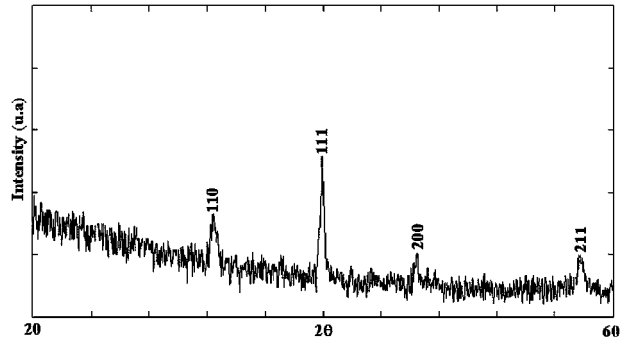

Figure 3 X-ray diffraction pattern of a 600-nm-thick $SrTiO_3$ thin film on a $Pt/Ti/SiO_2/Si(100)$ substrate annealed at 700°C.

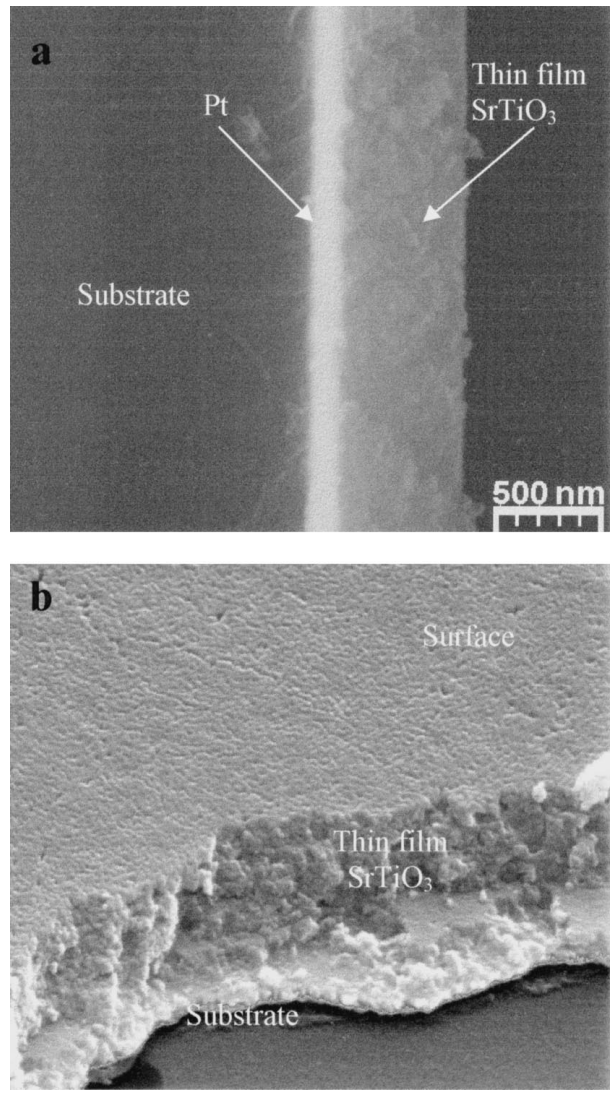

Figure 4 Cross-section and surface microstructure of $SrTiO_3$ thin films heat-treated at 700°C, carried out by SEM.

Fig. 3 shows the diffraction patterns of the film after a 2-hour heat treatment at 700°C. The pattern shown in Fig. 3 depicts a typical polycrystalline film. All the peaks are ascribed to a cubic perovskite structure. A further analysis of the XRD data indicated a lattice parameter of $a = 0.3903$ nm. This value is close to the bulk material ($a = 0.3905$ nm). These parameters are in agreement with the values found in the literature [19, 20] for $SrTiO_3$ thin films prepared by chemical or physical methods.

3.2. Surface morphology and microstructure

Fig. 4 shows the SEM photomicrograph of the cross-sectional and the microstructural surface view of $SrTiO_3$ thin film. Fig. 4a shows a thin film with a thickness of approximately 600 nm. Interfaces between deposition layers are clearly shown in this figure. Each layer displays a very dense, uniform and sharp interface.

AFM imaging was carried out in the contact mode, using a triangular shaped 200-micron long cantilever with a spring constant of 0.06 N/m. The scanning rate varied from 1 to 2 Hz and the applied force from 10 to 50 nN, depending on sample/tip interaction. Surface roughness (rms) was calculated using the equipment's software routine.

Average grain size and surface roughness of the $SrTiO_3$ thin film were also estimated using atomic force microscopy (AFM). Fig. 5 shows a three-dimensional and a two-dimensional image of an $SrTiO_3$ film

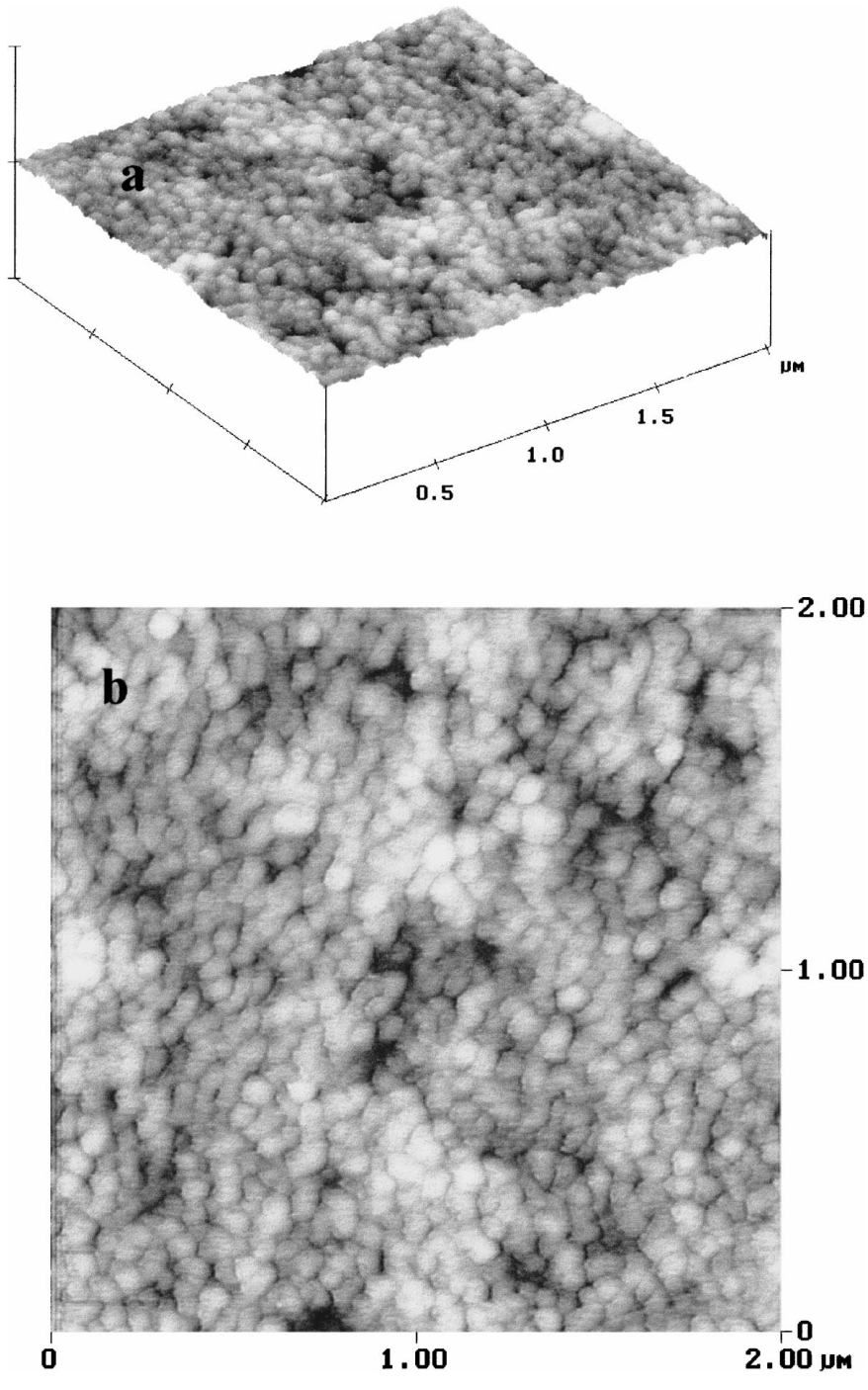

Figure 5 AFM 3D surface image of a 600-nm-thick $SrTiO_3$ thin film annealed at 700°C.

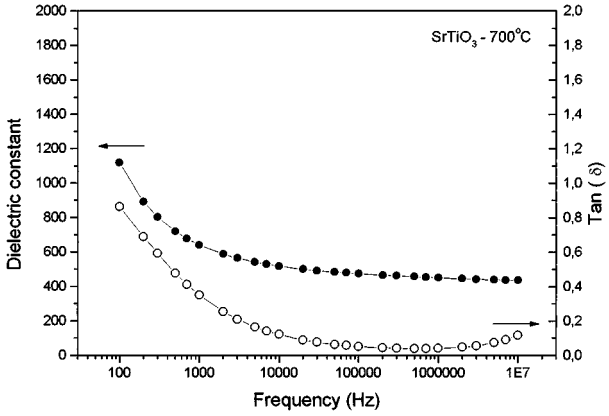

Figure 6 Dielectric constant and dissipation factor as a function of frequency for $SrTiO_3$ thin film heat treated at 700°C.

annealed at 700°C for 2 h. This film was characterized by a smooth surface with a uniform, crack-free microstructure and was densely packed, which is in agreement with the SEM analysis. The average grain size and the surface roughness were close to 70 nm and 2.5 nm, respectively.

3.3. Dielectric properties

The dielectric behavior was measured on the $SrTiO_3$ film in the MIM configuration. Fig. 6 shows the room temperature values for the dielectric constant and the dissipation factor for a $SrTiO_3$ film annealed at 700°C for 2 hours as a function of the frequency. It can be observed that the dielectric constant displays a slight frequency dependency for 600 nm-thick thin film. The dielectric constant and the dissipation factor, at a frequency of 100 kHz, were 475 and 0.050, respectively. The dielectric constant is higher than the value for the $SrTiO_3$ sintered ceramic [7] (about 300). Hofman *et al*. [21], on the other hand, obtained dielectric constant and dissipation factor values of up to 200 and 0.04, respectively, for 600-nm-thick $SrTiO_3$ film using the sol-gel process.

Dielectric constant values depend on several factors such as annealing temperature, bottom electrodes, composition and others [22]. However, the dielectric constants obtained here were higher than the values reported for $SrTiO_3$ films obtained by other techniques such as MOSD [23], sol-gel [19] and laser ablation [24], considering about the same thickness and MIM configuration. Table II lists some results for $SrTiO_3$ thin films prepared by other techniques.

The increased dielectric constant at the lower frequencies, as illustrated in Fig. 6, is believed to be related to interfacial polarization of space charges [25, 26]. The increase observed in the dissipation factor for frequency values above 10^6 Hz may be related to space charge conductivity effects. Moreover, the dielectric constant value measured with different electrodes varied by less than 3%, indicating a good degree of uniformity in film thickness.

Fig. 7 shows the Capacitance-Voltage (C-V) characteristic of the $SrTiO_3$ thin film obtained at 100 kHz by imposing a dc voltage $+7$ and -7 V. A typical paraelectric behavior is observed for this film. The behavior observed here is consistent with that observed by Kyeong *et al*. [27]

TABLE II Electrical properties of $SrTiO_3$ film according to literature

Processing Temp. °C	Dielectric Constant	Tan δ	Thickness nm	Deposition Method
600	225 (100 kHz)	0.14 (100 kHz)	1000	Laser ablation
700	225 (100 kHz)	0.008 (100 kHz)	800	MOSD
600	170 (100 kHz)	-	560	Sputtering
700	130 (100 kHz)	0.022 (100 kHz)	800	Sol-gel
650	239 (100 kHz)	-	1000	Laser ablation
700	475 (100 kHz)	0.050 (100 kHz)	600	This study

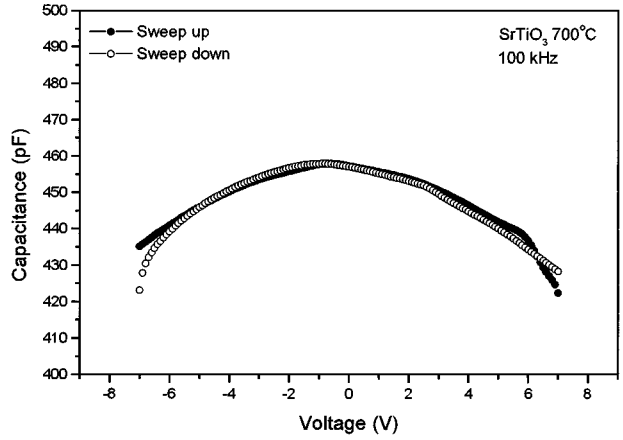

Figure 7 Capacitance-voltage characteristics of the $SrTiO_3$ thin film.

The very satisfactory dielectric behavior reported in this work is ascribed to the high microstructural quality and high chemical heterogeneity of the film obtained by the polymeric precursor method.

4. Conclusions

Polycrystalline, homogenous, and crack-free $SrTiO_3$ thin films were successfully prepared by the polymeric precursor method. The films were deposited on a $Pt/Ti/SiO_2/Si(100)$ substrate using the spin coating technique and a 700°C heat treatment in air. A smooth, dense surface was observed by SEM and AFM. These analyses revealed low surface roughness (even 2.5 nm) for the multilayered films. XRD results showed a polycrystalline film with a cubic structure and a lattice parameter of 0.3903 nm. The multilayer thin films consisted of fine grains of approximately 70 nm, with a film thickness of 600 nm.

Dielectric properties were measured using a MIM configuration. The $SrTiO_3$ thin films showed a paraelectric behavior and a dielectric constant of 475 and dielectric loss of 0.050 at 100 kHz. The results indicate that the films are within the dielectric constant range obtained by other techniques. Therefore, it can be inferred that our $SrTiO_3$ film is well suited for application in the planar capacitor layer in DRAMs as a material with a high dielectric constant. These results also suggest that the polymeric precursor method is appropriate to produce strontium titanate thin films with superior dielectric qualities.

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