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Preparation, microstructural and electrical characterization of $SrTiO_3$ thin films prepared by chemical route

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Abstract

Polycrystalline $SrTiO_3$ thin films having a cubic perovskite structure were prepared at different temperatures by the polymeric precursor method on platinum-coated silicon substrate. Crystalline films with uniform composition and thickness were prepared by spin-coating and the post-deposition heat treatment was carried out at different temperatures. The film showed good structural, dielectric, and insulating properties. Scanning electron microscopy (SEM) micrographs showed no occurrence of interdiffusion between the bottom electrode (platinum) and the film during post-annealing, indicating a stable interface between the $SrTiO_3$ and the bottom electrode. The dielectric constant and dissipation factor at a frequency of 100 kHz were 250 and 0.01, respectively, for a 360 nm thick film annealed at 600°C. The capacitance versus applied voltage characteristics showed that the capacitance was almost independent of the applied voltage. The *I–V* characteristics were ohmic in low fields and a Schottky emission and/or Poole-Frenkel emission were postulated in high fields. Room temperature leakage current density was found to be in the order of 10^{-7} A/cm^2 for a 360 nm thick film in an applied electric field of about 100 kV/cm. The charge storage density of 36 fC/μm^2 was obtained in an applied electric field of about 100 kV/cm. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Films; Perovskites; Spin coating; $SrTiO_3$

1. Introduction

Ferroelectric thin films have been investigated in recent years for application in memory cell capacitors for nonvolatile memories or dynamic random access memories (DRAMs).[1–6] Spontaneous polarization and its reversibility by an applied electric field are unnecessary for DRAMs, although a high dielectric constant with low leakage current is required. Among numerous ferroelectric materials, paraelectric strontium titanate ($SrTiO_3$) a cubic perovskite-type crystal, has attracted particular attention for application in dielectrics for dynamic random access memories (DRAM) because of its high dielectric constant, lack of fatigue or aging problems in the working range, good thermal stability and high compatibility with device processes.[7,8] Many investigators have studied deposition methods for these thin films and their electric properties. $SrTiO_3$ films have been prepared using sputtering, pulsed laser deposition, reactive coevaporation, and metallo-organic deposition (MOD).[9–12] However, these methods require a high deposition and/or post annealing temperature. On the other hand, polymeric precursor method-derived thin films[13–15] are very attractive candidates for a variety of new applications in microelectronics, e.g. DRAMs. Despite this fact, few reports have been published on the preparation of $SrTiO_3$ by the polymeric precursor method.[16] The main advantage this method offers is the easy production of pure, homogeneous, stoichiometric ceramic thin films that usually become polycrystalline at relatively lower temperatures than with other methods.

This work, which consisted of the examination of $SrTiO_3$ thin films deposited by the polymeric precursor method at different temperatures, resulted in 360 nm-thick $SrTiO_3$ film with a high dielectric constant, low leakage current, and high dielectric breakdown strength.

2. Experimental procedure

Fig. 1 outlines the flow chart of the $SrTiO_3$ synthesis used in this study. Titanium citrates were formed by

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dissolution of titanium isopropoxide in an aqueous 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 a polyesterification reaction. The molar ratio between the strontium and titanium cations was 1:1, the citric acid/metal ratio was set at 1.00, and the citric acid/ethylene glycol ratio was fixed at 60/40 (mass ratio).

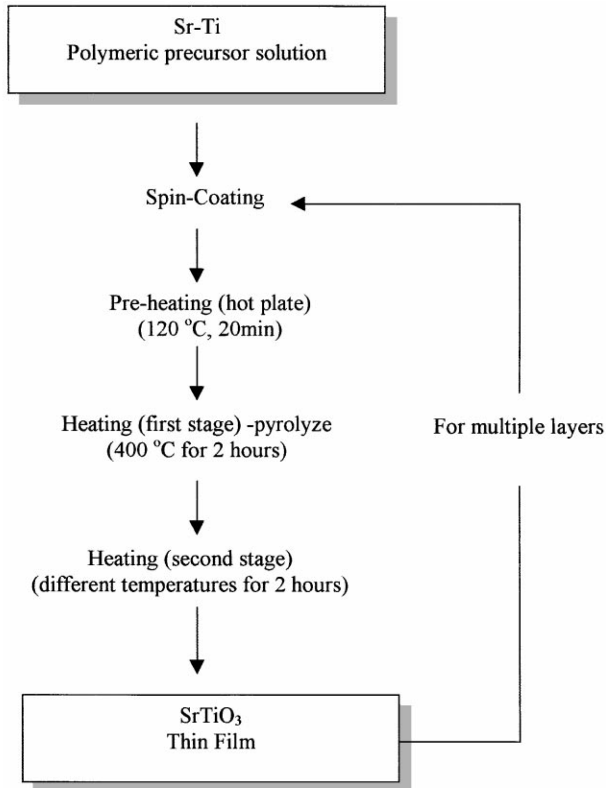

Fig. 1. Flow chart for polymeric precursor processing of $SrTiO_3$ thin film.

Platinum-coated silicon was used as the substrate, which was spin-coated by dropping a small amount of the polymeric precursor solution onto it. Rotation speed and spin time were fixed at 4500 rpm and 30 s, respectively. After deposition, each layer was dried at 120°C on a hot plate 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 different temperatures for 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 different temperatures before the next layer was deposited.

The $SrTiO_3$ films were structurally characterized by X-ray diffraction (XRD) (Cu K_α radiation) and the diffraction patterns recorded on a Siemens D5000 machine in a θ–2θ configuration, using a graphite monochromator. Microstructural characterization was performed by atomic force microscopy AFM to obtain a 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. Film thickness was measured by a thin film cross-section analysis made by SEM (Zeiss, DSM94OA).

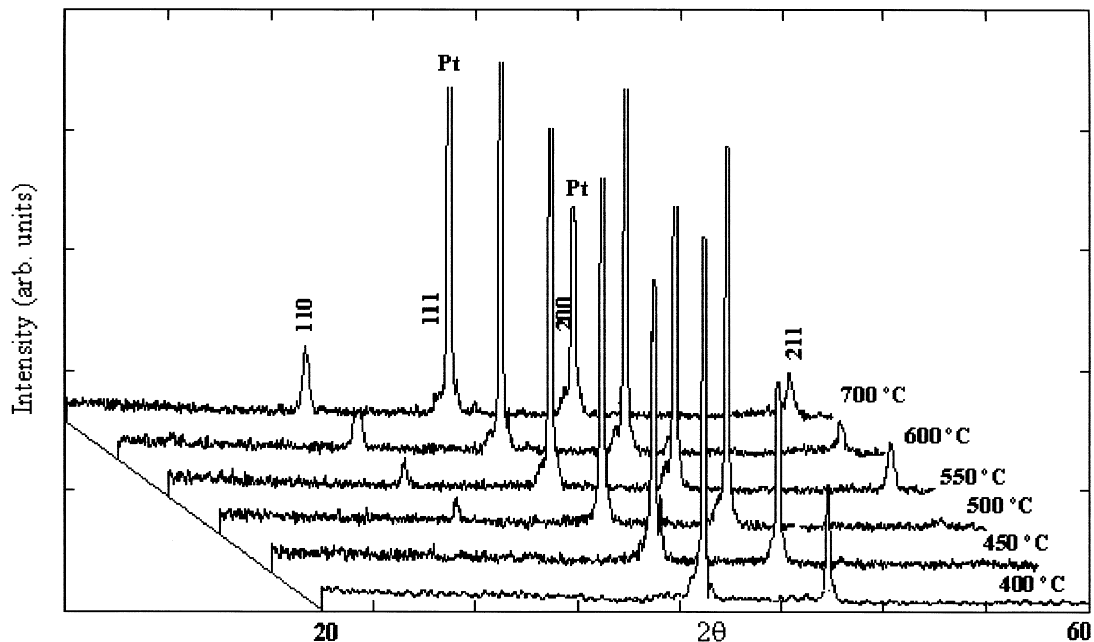

Fig. 2. X-ray diffraction patterns of $SrTiO_3$ thin films annealed at different temperatures.

To carry out the electrical measurements, 0.3 mm diameter gold electrodes were deposited by sputtering through a designed mask onto the film surfaces to form metal–insulator–metal capacitors (MIM). The dielectric properties were measured as a function of frequency using a Hewlett-Packard (4194A) impedance/gain phase analyzer.

The capacitance versus applied voltage characteristic was measured in the 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 to positive bias (*C–V* curves). Dielectric constant and dissipation factor values were measured at a frequency range of 100 Hz–10 MHz in 360-nm-thick films. *I–V* characteristics were measured with a Keithley 237 electrometer/source. All the measurements were taken at room temperature.

3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of polymeric precursor method-grown $SrTiO_3$ thin film deposited on platinum-coated silicon substrate and annealed at different temperatures for 2 h. A diffuse XRD pattern is observed at 400 and 450°C, indicating the formation of an inorganic amorphous precursor after the pyrolysis process. For temperatures higher than 450°C, begins the crystallization of the $SrTiO_3$ perovskite phase. No intermediate phase was observed which suggests a direct crystallization from the amorphous phase. This type of transformation was reported by Okumada and Komatsu[17] for $SrTiO_3$ films prepared by the sol-gel method. However, crystalline structure patterns were identified in the films heat treated above 600°C. Similar results also were reported by Leite et al.[18] for $Ba_{1-x}Sr_xTiO_3$ (BST) thin films prepared by Pechini process, where the characterization of these films showed that BST phase crystallizes at 600°C from an inorganic amorphous matrix and no intermediate crystalline phase was observed.

The diffractogram reveals well-defined peaks showing a good deal of crystallinity. The intensities of the peaks agree very well with those given in ASTM data cards (#5-634) for $SrTiO_3$, suggesting that the film was polycrystalline. All the peaks are ascribed to a cubic perovskite structure having an $a=b=c$ 3.90 Å lattice.

Fig. 3 shows the SEM image of a cross-section and the surface of the $SrTiO_3$ film prepared at 600°C. $SrTiO_3$ film thickness was 360 nm, each layer displaying a very dense, uniform and sharp interface as well as a granular fine grain microstructure. No interdiffusion between the platinum layer and the $SrTiO_3$ layer was observed in the SEM images. Additional investigations by cross-section analysis in transmission electron microscopic (TEM) and energy dispersive spectroscopy (EDS) for $SrTiO_3$ thin films prepared by the Pechini

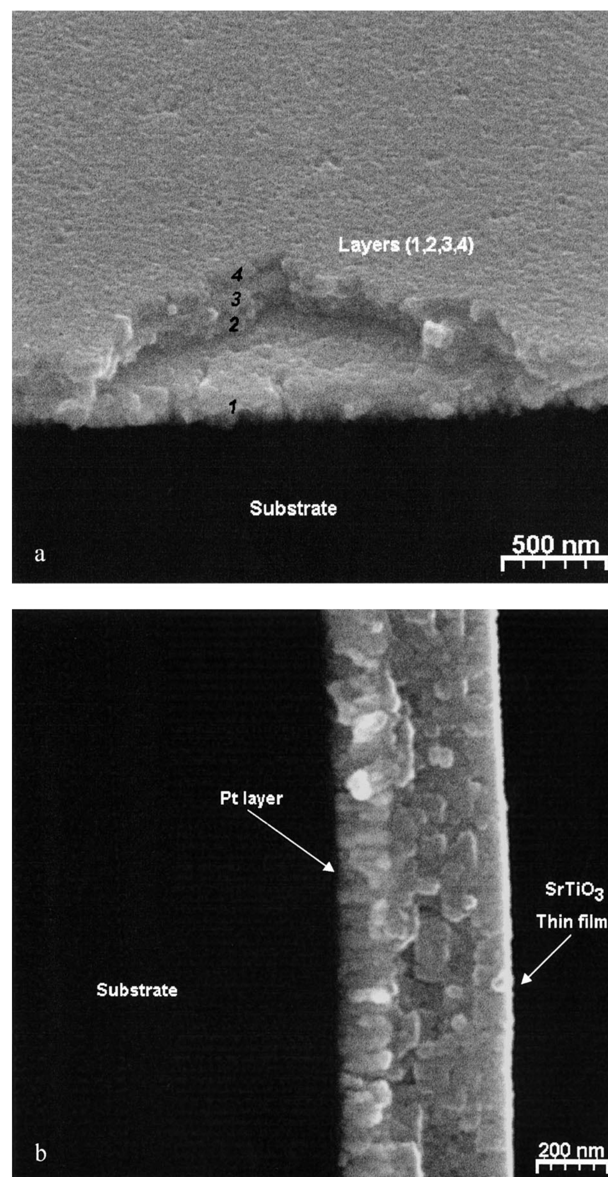

Fig. 3. SEM micrographs of $SrTiO_3$ film heat treated at 600°C: (a) SEM micrograph of surface morphology of $SrTiO_3$ film; (b) SEM micrograph of cross-sectional view of $SrTiO_3$ film.

process and heat treated at 700°C for 2 h confirmed that no interdiffussion between the platinum layer and the $SrTiO_3$ layer occurred. Similar results have also been reported for the $SrTiO_3$ films grown by Paek et al., obtained at 700°C by the rf-magnetron sputtering method.[19]

Average grain size and surface roughness of the $SrTiO_3$ thin film were also estimated using atomic force microscopy (AFM). Fig. 4 shows three-dimensional and two-dimensional images of a $SrTiO_3$ film annealed at 600°C for 2 h, which was characterized by a smooth surface with a homogeneous, crack-free, densely packed microstructure. Average grain size and surface roughness were close to 60 and 2.5 mm, respectively.

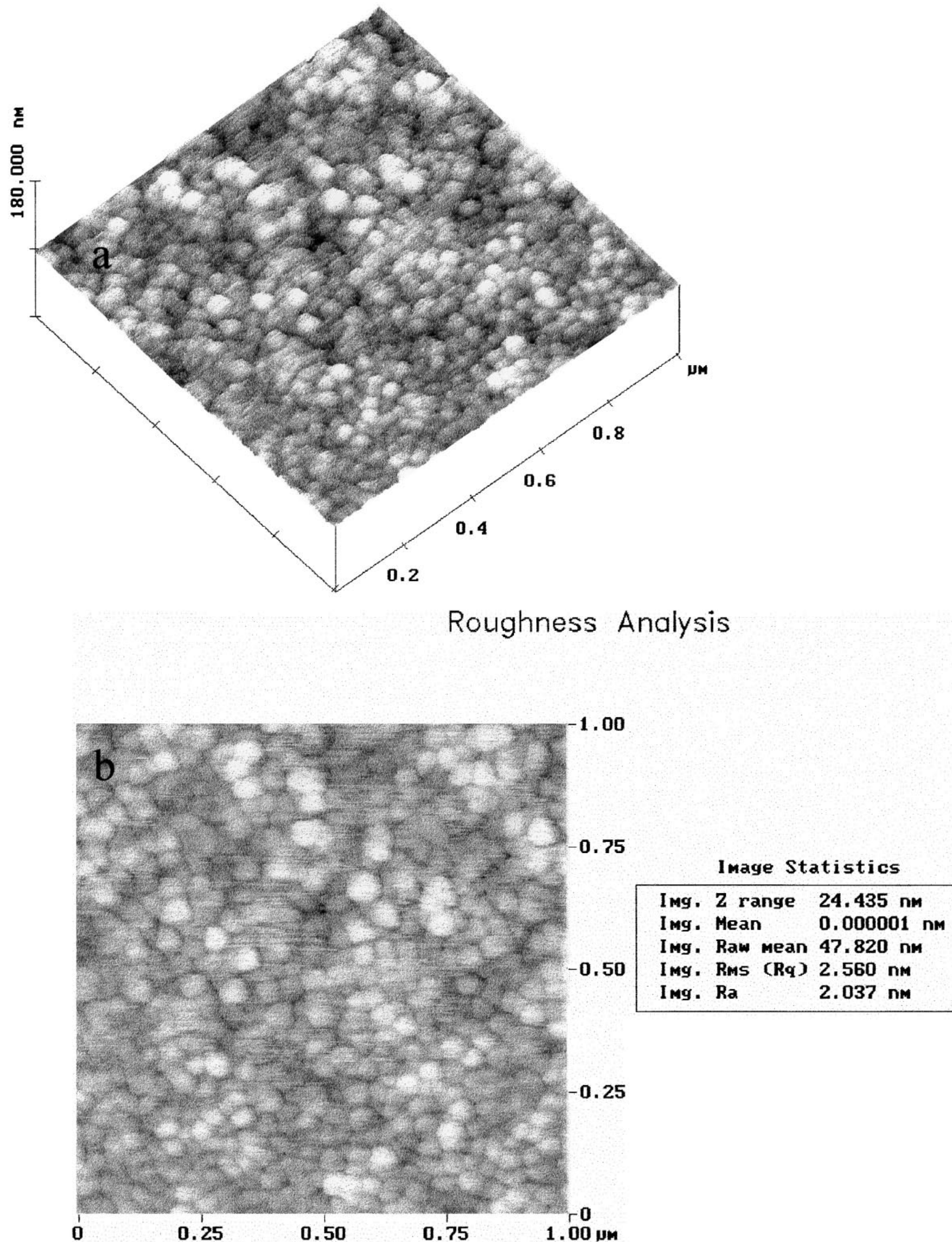

Fig. 4. Atomic force microscopy images of the $SrTiO_3$ thin film: (a) 3D image surface, and (b) 2 D image surface with result roughness analysis.

Fig. 5 gives the variation of the dielectric constant and dissipation factor (tan δ) as a function of applied frequency. The dielectric constant displays an approximate decline of 13% with increasing applied frequency from 100 Hz to 1 MHz, a much lower value than the 30% decrease reported by Rao and Krupanidhi for $SrTiO_3$ films grown by pulsed excimer laser.[20] As shown in Fig. 5, the dielectric constant and dissipation factor for a 360 nm film at a frequency of 100 kHz were 250 and 0.01, respectively. The dielectric constant at a frequency of 1 MHz was 241, higher value than those reported by Nam and Kim[21] for films deposited by sputtering and by

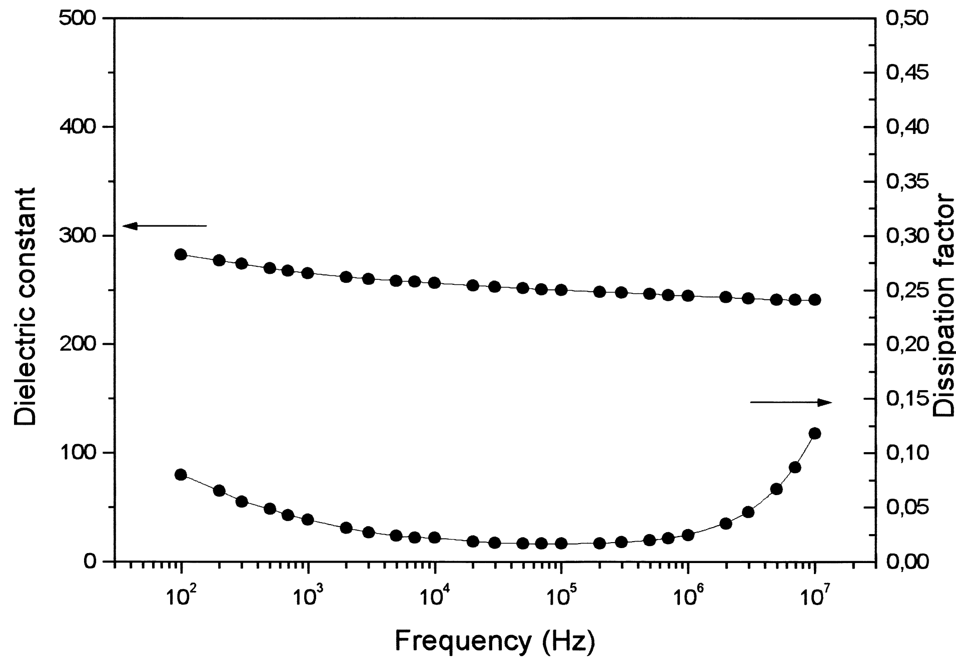

Fig. 5. Dielectric constant and dissipation factor as a function of applied frequency for $SrTiO_3$ thin film heat treated at 600°C.

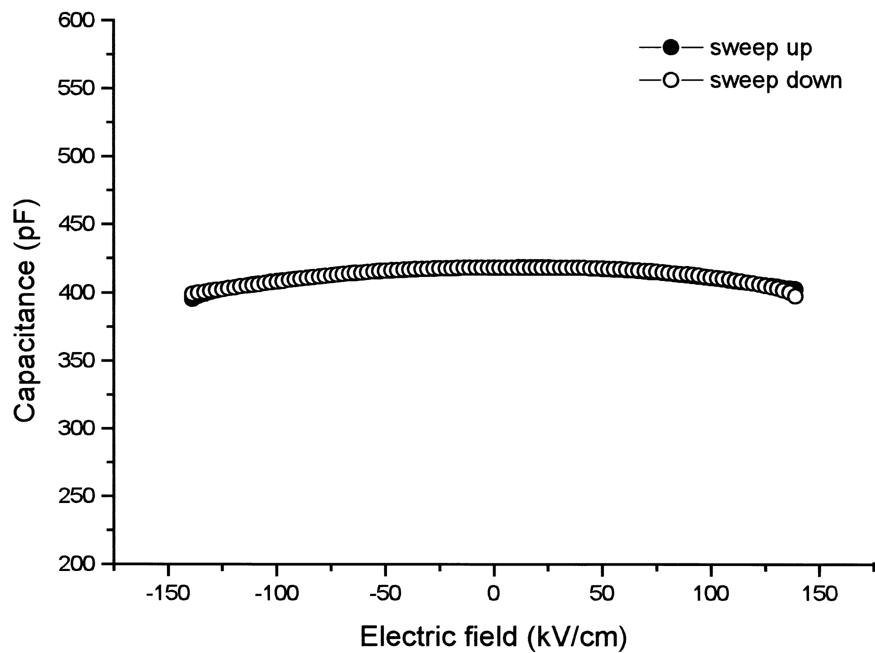

Fig. 6. Capacitance versus applied voltage characteristics of paraelectric thin film. $SrTiO_3$ thin film heat treated at 600°C.

Thomas et al.[22] for films prepared by sol-gel method, which showed lower dielectric constants of 140 and 105 at 1 MHz, respectively. In other work $SrTiO_3$ films prepared by sol-gel method[23] and annealed at 700°C showed a dielectric constant of 131 at a frequency 1 kHz. Furthermore, Joshi and Krupanidhi[12] reported for a 800 nm thick $SrTiO_3$ film, deposited by metallorganic solution at 600°C, a dielectric constant of about 225 at 100 kHz. In addition, $SrTiO_3$ films prepared by the sol-gel method[17] at 650°C had a dielectric constant of about 60, which was lower than that for $SrTiO_3$ ceramics, which was attributed to the existence of an amorphous layer in the interface on the substrate.

The capacitance of the film, shown in Fig. 6, was measured against a dc bias at 100 kHz. There was no appreciable change in capacitance with applied voltage. This result indicated the paraelectric properties of $SrTiO_3$ thin film at room temperature. Thus, the film shows good

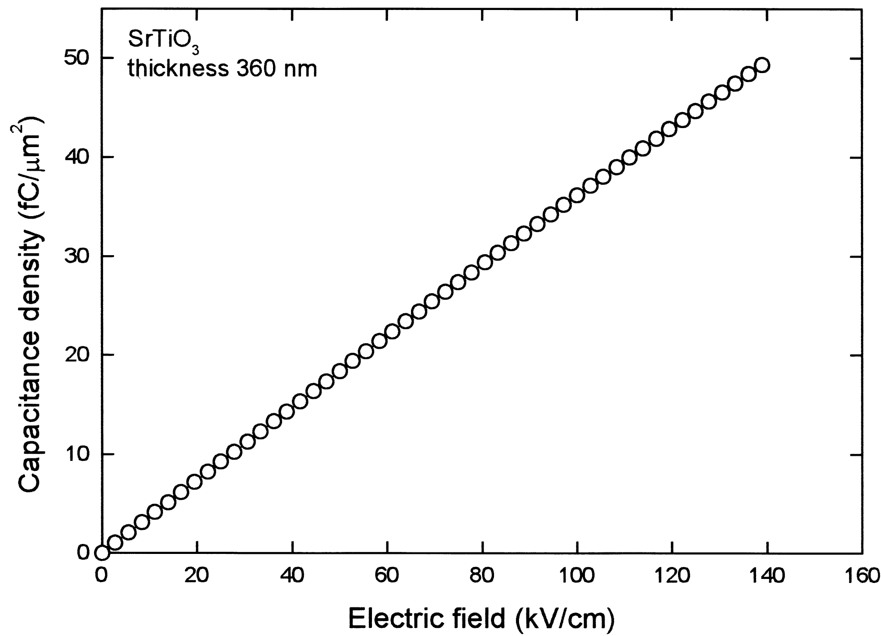

Fig. 7. Charge storage density versus the applied electric field for $SrTiO_3$ thin film.

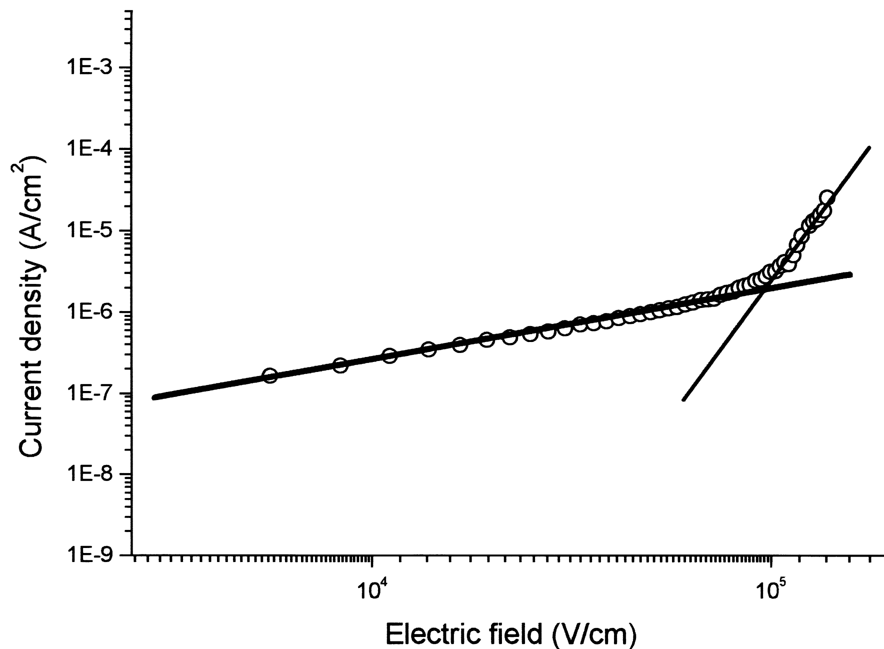

Fig. 8. Typical log (*J*) versus log (*E*) curve for $SrTiO_3$ thin film prepared by the polymeric precursor method.

properties for dynamic random memory (DRAM) applications, which requires a flat dependence of capacitance on applied voltage. Dielectric material for DRAM applications should, however, have a high charge storage density and a low current leakage density. The charge storage density of $SrTiO_3$ thin film was estimated from the capacitance-voltage characteristics shown in Fig. 6, using the relationship:

$$Q_c = \varepsilon_o \varepsilon_r E, \quad (1)$$

where E is the applied electric field, ε_o is the free space permittivity, and ε_r is the dielectric constant calculated for the $SrTiO_3$ film shown in Fig. 5. Fig. 7 shows the variation of charge storage density of $SrTiO_3$ films with applied electric field, where one can observe a linear relationship between the applied electric field and the charge storage density. This behavior is similar to other linear dielectrics.[24] The charge storage density was estimated at 36 $fC/\mu m^2$ in an applied field of 100 kV/cm. These values appear to be consistent with the projected

requirements for DRAMs memories Fig. 8 shows the current-voltage characteristics of the MIM capacitor structure with a 360 nm thick $SrTiO_3$ film measured with a voltage step of 0.1 V and elapsed time of 1.0 s. In the log J versus log E plot, the leakage current density increases linearly with the external electric field in the region of the low electric field, with a slope of about 0.88, indicating an ohmic-like conduction mechanism. Above a critical field, the leakage current density increases non-linearly since the current conduction is governed by another emission mechanism (either Schottky or Pool-Frenkel). In the high field region, the log(J) vs log(E) curve presents a slope higher than 6. The leakage current levels of the $SrTiO_3$ film obtained by the polymeric precursor method was about of 10^{-7} A/cm^2 at an applied electric field of 100 kV/cm.

4. Conclusions

Polycrystalline $SrTiO_3$ thin films were prepared by the polymeric precursor method on Pt/Ti/SiO_2/Si substrates at different temperatures. The $SrTiO_3$ thin films prepared at 600°C consisted of fine grains of approximately 60 nm, with a thickness of 360 nm. AFM analysis revealed low surface roughness (=2.5 nm) and a densely packed surface for the multilayer films. SEM micrographs showed no interdiffusion between the bottom electrode (Platinum) and $SrTiO_3$ thin film during heat treatment at 600°C, indicating a stable interface between $SrTiO_3$ and Pt. A dielectric constant of 250 and a low dissipation factor of 0.01 were observed at a frequency 100 kHz. The charge storage density and leakage current density were 36 fC/μm^2 and 10^{-7} A/cm^2, in an electric field of about 100 kV/cm, respectively. Further studies of leakage current of the capacitor indicated an ohmic conduction in the low field regions and Schottky emission and/or Poole-Frenkel emission in the high field regions. The high dielectric constant, low dielectric loss (dissipation factor), high charge storage density and good capacitance versus applied voltage characteristics suggest that $SrTiO_3$ thin films prepared by the polymeric precursor method are attractive as material for DRAM applications.

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