Characteristics of post-annealed SrTiO$_3$ thin films prepared by mirror-confinement-type ECR plasma sputtering

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Received 15 November 2000; revised 22 November 2000; accepted 24 November 2000

Abstract

SrTiO$_3$ films were synthesized on Pt/Ti/SiO$_2$/Si multilayer substrates by mirror-confinement-type ECR plasma sputtering without substrate heating. All films were found to be well crystallized at a substrate temperature below 450 K. A low temperature post-annealing of the films by electromagnetic-wave radiation drastically improved the crystallographic and electric properties of Pt/SrTiO$_3$/Pt/Ti/SiO$_2$/Si capacitors. The crystallinity of the films indicated little variation by post-annealing, but irradiation of electromagnetic wave was confirmed to be effective for decreasing the post-annealing time and temperature. The electric properties of films annealed without Pt upper electrodes were better than those with them, and the film dielectric constant reached a value of 260, which is nearly equal to the bulk one, at an annealing temperature of 573 K. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: SrTiO$_3$; Post-annealing; Low temperature synthesis; Electromagnetic-wave radiation; Mirror-confinement-type ECR plasma sputtering

1. Introduction

Perovskite materials of the ABO$_3$-type, such as strontium titanate (SrTiO$_3$), barium titanate (BaTiO$_3$) and barium strontium titanate ((Ba,Sr)TiO$_3$) have been utilized in the information technology (IT) industry. Among them, the SrTiO$_3$ thin film is one of the candidate dielectric material for capacitors in the next generation dynamic random access memory (DRAM) with 1 Gbit density or higher, as well as on monolithic microwave integrated circuits (MMICs) due to its high dielectric constant ($\varepsilon_r \sim 300$) [1]. These films have been synthesized by several processes such as RF magnetron sputtering [2], divergent magnetic field type electron–cyclotron-resonance (ECR) plasma sputtering [3], metalorganic chemical vapor deposition (MOCVD) [4], molecular beam epitaxy (MBE) [5], pulsed laser deposition (PLD) [6], and ion beam sputtering [7].

In these processes, a high temperature post-annealing above 900 K is usually required for the crystallization of these films, in addition to the substrate temperature during deposition. From the viewpoint of utilization of thermally unstable substrates such as polymer sheets and metals with low melting point, it is important to deposit films at a temperature as low as possible.

We have deposited SrTiO$_3$ thin films without substrate heating, using mirror-confinement-type ECR plasma sputtering system in a low-pressure environment of $2.7 \times 10^{-2}$ Pa, and applied electromagnetic wave radiations for low temperature post-annealing of the films [8–10]. By the conventional post-annealing method, the crystallization temperature of as-deposited amorphous films on Si substrates, which was synthesized at a substrate temperature below 450 K, was found to be about 673 K. Application of an electromagnetic wave radiation for post-annealing of these films could decrease the crystallization temperature to a value of 573 K. However, as-deposited films on Pt/Ti/SiO$_2$/Si substrates were found to be sufficiently crystallized even without post-annealing.

In this study, we have investigated the effects of electromagnetic wave radiation for post-annealing on the crystallographic and electric properties of the SrTiO$_3$ thin films synthesized on Pt/Ti/SiO$_2$/Si multilayer substrates by the mirror-confinement-type ECR plasma sputtering.

2. Experimental

SrTiO$_3$ thin films are deposited on Pt/Ti/SiO$_2$/Si substrates using the mirror-confinement-type ECR plasma sputtering system developed by us as shown in Fig. 1. The
deposition conditions of SrTiO₃ thin films are summarized in Table 1. SiO₂ layer was grown on a p-type Si (100) substrate by thermal oxidation method. Bottom Pt and Ti electrodes with 100 and 50 nm thickness, respectively, were deposited at room temperature (RT) using an ion beam sputtering method. Upper Pt electrodes were fabricated by a lift-off technique, where a stainless steel shadow mask with circular holes of 0.00094 cm² area was used. Typical film thickness is fixed at 200 nm.

As-deposited thin films were annealed using a 28 GHz millimeter-wave heating equipment (FGS-10-28, Fuji Denpa Kogyo). Heating and cooling rates for post-annealing were fixed at a condition of 20 K/min. The temperature was measured by a K-type thermocouple contact to the film surface.

Film microstructures were identified by glancing angle X-ray diffraction (XRD, MAC Science Co. Ltd) method using a monochromatized CuKα radiation. The film morphology was observed using a field-emission-type scanning electron microscopy (FE-SEM, HITACHI Co.). The film composition was analyzed by Rutherford backscattering spectrometry (RBS, Charles Evans and Associates (CEA)) technique. In the RBS analysis, a 2.281 MeV He⁺ ion beam was used and backscattered particles were detected at a scattering angle of 160°. The data were analyzed using the HYTRA software package [11]. Chemical compositions were evaluated by X-ray photoelectron spectroscopy (XPS, Surface Science Instruments) with an AlKα radiation (1486.6 eV). The X-ray spot size was 250 × 1000 µm². Narrow scan spectra of all interested regions were recorded with a 50 eV pass energy to qualify the surface composition and identify the chemical binding state. All samples were sputtered to 20 nm in depth from the sample surface by Ar ions with a sputtering rate of 0.08 nm/s. Film polarization and dielectric constant were measured through electric field characteristics using a ferroelectric test system (Radiant Technology Inc.). Capacitance and dielectric constant measurements were carried out at room temperature with an LCR meter (HIOKI) in the frequency range between 100 Hz and 100 kHz.

### Table 1
Sputtering conditions for SrTiO₃ thin films

| Target material     | Sintered SrTiO₃ |
|---------------------|----------------|
| Base pressure of system | 1.1 × 10⁻³ Pa   |
| Sputtering pressure | 2.7 × 10⁻³ Pa   |
| Sputtering gas      | Ar + O₂ mixture |
| Target-to-substrate distance | 80–160 mm |
| Sputtering time     | 60 min         |
| Deposition rate     | 3.3 nm/min      |
| Substrate           | Pt(100 nm)/Ti(50 nm)/SiO₂/Si |
| Microwave power     | 200 W (2.45 GHz, 875 G) |
| RF power on target  | 200 W (13.56 MHz) |
| Substrate temperature | Below 450 K   |
| Upper electrode     | Pt (100 nm)     |

Fig. 1. Schematic diagram of experimental apparatus.

3. Results and discussion

Fig. 2 shows the variation of XRD (110) peak profiles of as-deposited films at various composition ratios of Sr/Ti. We can see that they are crystallized without the substrate getting heated. The peak gets shifted to a lower angle when Sr/Ti is increased, compared with a value of the bulk one (2θ = 32.397°), which means the lattice parameter becomes larger when Sr/Ti > 1. These non-stoichiometric SrTiO₃ films (x < 1 or x > 1) are also interesting materials, sometimes revealing superconductivity [12]. It is reported [13] that the excess Sr is easy to form a Ruddlesden–Popper phase, SrO(SrTiO₃)ₓ with a Sr–O plane, and the lattice parameter becomes larger because of the distortion in the vicinity of the Sr–O plane between SrTiO₃ sublattices. From
this report, we consider the formation of a Sr–O plane within the non-stoichiometric SrTi$_{1-x}$O$_x$ films ($x < 1$) as one of the causes of the observed peak shift. However, it is reported [14] that the existence of excess Sr at a condition of Sr/Ti > 1 and excess Ti at Sr/Ti < 1 induces the oxygen vacancy with two compensation electrons ($V''_O$) from the viewpoint of defect chemistry, expressed as depicted in Kröger–Vink notation:

\[
\text{SrO} = V''_{\text{Sr}} + \text{Sr} + O_O + 2V''_O \quad (\text{Sr/Ti} > 1)
\]

\[
\text{TiO}_2 = V''_{\text{Ti}} + \text{Ti} + 2O_O + V''_O \quad (\text{Sr/Ti} < 1)
\]

The stoichiometric SrO thin films as capacitors are preferred to be synthesized because oxygen vacancy may act as an electron trap site, which causes poor electrical properties of capacitors. In this sense, the post-annealing is usually recommended [15] for suppressing the oxygen vacancy generated at the interface with the Pt electrodes, regardless of the crystallization of the as-deposited films.

Fig. 3 shows the XRD patterns of SrTiO$_3$ films at various post-annealing temperatures for 60 min with 28 GHz millimeter-wave radiations. We can clearly find that as-deposited films have well-crystallized structure without post-annealing and peak profiles seem to show no
remarkable variation up to the post-annealing temperature of 673 K.

Fig. 4 shows the variation of the XRD (110) peak profiles for various post-annealing temperatures. The peak position and crystallite size are also shown for various post-annealing temperatures for 60 min with 28 GHz millimeter-wave radiation. The crystallite size \( t \) was calculated by Scherrer’s formula \( t = K \lambda / (\beta \cos \theta) \), where \( K \), \( \lambda \), \( \beta \) and \( \theta \) denote the Scherrer constant (= 1), wavelength of CuK\( \alpha \) radiation, integrated width of the peak profile and Bragg angle of diffraction peak, respectively. In this equation, the crystallite size is assumed to have a Gaussian distribution with cubic phase.

We find in the figure that the peak is shifted a little toward the angle of bulk SrTiO\(_3\) (2\( \theta \) = 32.397\(^\circ\)) and the crystallite size slightly increases to a value of 11–12 nm on increasing the post-annealing temperature. This size corresponds well with the result of FE-SEM observation [10], where the film indicates a granular structure. The electrical properties of the films with granular grains are considered to show better quality than those with columnar one [15–17].

Fig. 5 shows the variation of the film polarization characteristics as a function of the applied electric field for various post-annealing conditions. In this figure, first- and second-annealing implies the post-annealing without and with Pt upper electrodes on the film, respectively. All films can clearly be identified to be paraelectric states by the linearity of polarization. The polarization of films by first-annealing is remarkably higher than those by second-annealing. It is reported [18] that the electric properties of post-annealed barium strontium titanate ((Ba, Sr)TiO\(_3\)) films by the conventional method with Pt upper electrode have been improved, because the oxygen which is trapped on the surface of the (Ba, Sr)TiO\(_3\) films can be diffused to Pt electrodes during post-annealing. Our result is contradictory, partly because the films with Pt upper electrodes will not be post-annealed uniformly by the millimeter-wave radiation due to its selective absorption to the electrode with appearance of local overheating of the film.

Fig. 6 shows the variation of the dielectric constant of as-deposited and first-annealed SrTiO\(_3\) films as a function of the applied electric field strength at the single triangle wave of 50 ms pulse width. The annealing temperature is 573 K. It is hardly affected with the electric field within the range of 5–25 MV/m. Moreover, the dielectric constant of post-annealed films has a high value of 260, which is comparable with the bulk one, whereas the as-deposited thin films reveal only 70, while the dielectric constant as a function of the wave frequency also does not indicate any variation.

The electric properties of post-annealed films at 673 K, however, could not be measured. The film surface changed its color from pink to blue with non-uniformity after post-annealing. At this high temperature, the composition ratio Sr/Ti in the film is considered to decrease and Ti ions in the film are reduced and oxidized [19–21] by diffusion of Ti atoms through the Pt grain boundary due to Pt catalytic behavior.

Fig. 7 shows the variation of the XRD (110) peak profile, its peak position and crystallite size of SrTiO\(_3\) films, post-annealed for various post-annealing times. The peak position maintains almost no variation for all post-annealing times and we demonstrate that the electric properties of films are possible to be improved within a remarkably short post-annealing time by using the electromagnetic wave radiation.

4. Conclusions

SrTiO\(_3\) thin films were synthesized on Pt/Ti/SiO\(_2\)/Si
substrates at low substrate temperatures by mirror-confinement-type ECR plasma sputtering. As-deposited thin films were found to have well-crystallized phases at a low deposition temperature of 450 K having fine granular structures with crystallite size of about 11–12 nm. The electric properties of the prepared Pt/SrTiO$_3$/Pt/Ti/SiO$_2$/Si capacitors were improved by post-annealing using millimeter-wave radiation with a dielectric constant little affected by the applied electric field strength (5–25 MV/m) and its frequency (100–100 kHz). The dielectric constant of films post-annealed without Pt upper electrode reached to about 260, and application

![Graph](image1)

**Fig. 5.** Film polarization as a function of the applied electric field for various post-annealing conditions.

![Graph](image2)

**Fig. 6.** Variation of the dielectric constant with electric field strength for as-deposited and first-annealed thin films.
of millimeter-wave radiation for post-annealing was found to improve the film electric properties even by a short time post-annealing as compared with the conventional one.

Acknowledgements

The authors would like to thank Drs Y. Makino and Y. Setsuhara for their continuous support and fruitful discussions. They also wish to thank Dr M. Kumagai, Kanagawa Industrial Technology Research Institute for his helpful discussion. Thanks are also due to Dr J.L. He for deposition of Pt and Ti, and Mr T. Ueno for using electromagnetic-wave radiation. They greatly acknowledge Mr H. Saito and Ms M. Suzuki, Kanagawa High Technology Foundation (KTF) for FE-SEM observation of film morphology and XPS analysis of film composition, respectively.

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