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Permittivity Enhancement of Mechanically Strained SrTiO₃ MIM Capacitor

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The possibility of strain engineering on SrTiO₃ high-k insulator was discussed. The tensile strain on SrTiO₃ thin films increased dielectric constant, and as a frequency became higher, the increment of dielectric constant increased. The mechanism of the tensile strain-induced capacitance increase was also discussed. The tensile strain reduced a damping of titanium-oxygen oscillator in SrTiO₃ film, and titanium-oxygen dipole moment was increased.

Introduction

According to the scaling rule of ULSI miniaturization, dynamic random access memory (DRAM) technologies demand the new high-k materials that have an equivalent-oxide-thickness (EOT) of < 0.5 nm with the high reliabilities. The surveys of DRAM high-k material and deposition processes have been widely carried out. As a candidate of the next DRAM high-k material, titanate perovskite materials have been investigated. Especially in titanate perovskite materials, SrTiO₃ and (Ba, Sr)TiO₃ particularly have been investigated because of its high dielectric constant. For radio frequency integrated circuits (RFICs), the area of the passive RF metal-insulator-metal (MIM) capacitor in a chip relatively grows with the scaling down of the metal-oxide-semiconductor field effect transistors (MOSFETs), and it is necessary to increase the dielectric constant of RF capacitor for smaller RFICs. The SrTiO₃ thin film for a high performance RF MIM capacitor was also investigated [1].

Elastic strain-induced increase of dielectric constant on (Ba, Sr)TiO₃ film doped with Y (Yttrium) was reported [2]. Compressive strain in the (Ba, Sr)TiO₃ film reduced dielectric constant, and Y-doping was applied to suppress the compressive strain and increase dielectric constant. Effect of iron doping of (Ba, Sr)TiO₃ was also reported [3]. Iron ion was substituted for titanium, and dielectric constant was increased. In a different perspective, strain engineering has been a one of the important issues in front end process of CMOS technologies, e.g., strained-induced subband structure engineering in Si MOSFET [4-5]. Mechanically applied uniaxial strain on CMOS circuit was reported [6]. By use of the four-point bending method, surface strain of up to 0.058 % was produced, and enhancement of drain current and circuit performance were shown.

In this work, effect of uniaxial tensile strain applied mechanically on SrTiO₃ thin film was investigated, and we discussed the mechanism of strain-induced dielectric constant enhancement.

Experiments

Sample preparation and experimental setup were as follows. A SrTiO₃ thin film was deposited by metal-organic chemical vapor deposition (MOCVD) on a sputter-deposited Pt (200 nm) /TiOx (20 nm)/ SiO₂ (400 nm) / silicon substrate. The precursors of the SrTiO₃ MOCVD were bis(2,2,6,6-methylethyltetramethyl-3,5-heptanedionato) strontium [Sr(METHD)₂], and methylpentanediol bis(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium [Ti (MPD)(THD)₂] with a solvent of ethylcyclohexane. The SrTiO₃ film was deposited at a temperature of 525 °C in a MOCVD reactor. The stoichiometry of the SrTiO₃ film was Sr/Ti = 50/50. The thickness of the SrTiO₃ film was 100 nm. Pt top electrode with a thickness of 180 nm was deposited on the top SrTiO₃ film using RF magnetron sputtering with a screen mask of 2 mm in diameter. Crystallinity of the SrTiO₃ film was measured by out-of-plane, and in-plane x-ray diffraction (XRD). Leakage current and dielectric properties of the SrTiO₃ film were investigated using Agilent 4156C precision semiconductor parameter analyzer, and Agilent 4284A LCR meter, respectively. Strain apparatus was installed in CASCADE Microtech summit probe station. By use of a strain apparatus in a probe station, precise measurements on electrical properties of the strained SrTiO₃ film were carried out.

In the capacitance-voltage measurement, the DC bias voltage V_{DC} on the SrTiO₃ MIM capacitor was varied from -2.0 V to +2.0 V at 0.05 V interval, corresponding electric field was from -0.2 MV/cm to +0.2 MV/cm, and the amplitude V_{osc} of signal voltage was fixed to 0.5 V, and the frequencies $\omega/2\pi$ of signal voltage were 30, 100, 300, and 500 kHz. The total applied voltage on the SrTiO₃ MIM capacitor was $V_{DC} + V_{osc} e^{i\omega t}$.

Characteristics of MOCVD SrTiO₃ thin films

The crystallinity of the SrTiO₃ thin film was measured by out-of-plane, and in-plane XRD. Figure 1 shows the results of XRD measurement. In the out-of-plane XRD spectrum, the strong peak of SrTiO₃ (200) at 2theta of 46.45 ° was observed, on the other hand, in the in-plane XRD spectrum, the peak of SrTiO₃ (110) at 2theta of 32.33 ° was dominantly observed. These results showed that the SrTiO₃ thin film had a crystallinity of (100) in the depth direction of the film, and also had a uniform crystallinity in the surface

Figure 1. X-ray diffraction pattern of the SrTiO₃ thin films: (a) out-of-plane measurement and (b) in-plane measurement.

direction, for example, in this measurement, the (110) peak was observed. In the in-plane XRD spectrum, the (200) peak was observed at a 2theta of 46.42 °, corresponding lattice distance was 0.1065 nm, on the other hand, in the out-of-plane XRD measurement, the (200) peak was observed at a 2theta of 46.45 °, corresponding lattice distance was 0.1064 nm. These results showed that the lattice distance of surface direction was slightly longer than that of depth direction.

The leakage current density of SrTiO₃ MIM capacitor was 1.51×10^{-6} and 2.77×10^{-6} A/cm² at bias electric fields of +0.10 and +0.20 MV/cm, respectively. This result showed that the MOCVD SrTiO₃ film had a good performance for DRAM high-k insulator.

Tensile Strain on SrTiO₃ MIM capacitor

Figure 2 shows a schematic diagram of the two-point bending method. The sample wafer with the SrTiO₃ film was installed on the bending apparatus and uniaxial tensile stress was mechanically applied, and the surface strain was produced on the SrTiO₃ film. Here the surface strain was estimated by the equation:

$$\zeta = \frac{\Delta L}{L} \bigg|_{\text{Surface}} \cong \frac{T \cdot \Delta y}{L^2}, \quad [1]$$

where T is a thickness of silicon substrate, and L is a length of sample from supporting point of substrate mounting, to the point that is strain forced, and Δy is a displacement of the strained-forced point of silicon substrate. This surface strain ζ corresponding to the elastic strain tensor e_{ij} is a diagonal element e_{xx} , and the elastic strain tensor is defined by the equation $e_{ij} = (\partial_i u_j + \partial_j u_i) / 2$, where u_i is a displacement of a position x_i : $x_i \rightarrow x_i + u_i$.

The results of capacitance-voltage measurements were summarized in Fig. 3. In this figure, the capacitance axis was converted to dielectric constant. The value of dielectric constants in Fig. 3 was average value from -2.0 V to +2.0 V in each measurement. At a low frequency of 30 kHz, after tensile strain was applied, the dielectric constant remained at a same value. At a high frequency of applied voltage, the effect of the tensile strain

Figure 2. Schematic diagram of two-point bending method used for applying uniaxial tensile strain on the SrTiO₃ thin films.

Figure 3. Tensile strain effect on dielectric constant of the SrTiO₃ thin films. After the tensile strain forced, the dielectric constant became larger.

appeared, and dielectric constant was increased. At a frequency of 500 kHz, the dielectric constant of the unstrained SrTiO₃ was 71.49, while after the tensile strain forced, and the dielectric constant became larger and was 90.66. As the frequency was increased, the dielectric constant became smaller. At a frequency of 30 kHz, the unstrained SrTiO₃ thin film had a dielectric constant of 169.38, and at 500 kHz it became 71.49.

Tensile Strain and Ion Dynamics

Here, we discussed the effect of the tensile strain on SrTiO₃, especially the relation between the strain and ion dynamics. In SrTiO₃ film, titanium ion and oxygen ion form ionic dipole moment, and contribute to high dielectric constant. The schematic diagram of the titanium-oxygen dipole moment is shown in Fig. 4 (a). When external electric field is applied to SrTiO₃ film, titanium ion moves and oscillates against oxygen ion plane. This dynamics is represented by a simple harmonic oscillator under external electric field as shown in Fig. 4 (b). Titanium ion and oxygen ion plane has a harmonic interaction with a relative distance z , the equation of motion is given by the equation:

$$M_{ion} \frac{d^2 z}{dt^2} + 2M_{ion} \Gamma \frac{dz}{dt} + M_{ion} \omega_0^2 z = Z_{ion} e E_0 \exp(i\omega t), \quad [2]$$

where M_{ion} is an ion mass, Γ is a damping coefficient, ω_0 and Z_{ion} are eigenfrequency and valence of ion, respectively. After solving this equation, the polarization $P = Z_{ion} e N_{ion} z$ is obtained, and the dielectric constant is derived as

$$\varepsilon = 1 + \frac{e^2 Z_{ion}^2 N_{ion}}{\varepsilon_0 M_{ion}} \frac{1}{(\omega_0^2 - \omega^2) + i2\Gamma\omega}, \quad [3]$$

and the real part of dielectric constant is given by the equation:

Figure 4. Schematic diagram of titanium-oxygen polarization in the SrTiO₃ thin films: (a) polarized titanium-oxygen configuration in the SrTiO₃ perovskite structure, and (b) the corresponding harmonic oscillator.

$$\frac{1}{k-1} = C^{-1} \frac{(\omega_0^2 - \omega^2)^2 + 4\Gamma^2 \omega^2}{\omega_0^2 - \omega^2}, \quad [4]$$

where k is the real part of the dielectric constant ε , and C is a constant coefficient $C = (e^2 Z_{ion}^2 N_{ion}) / (\varepsilon_0 M_{ion})$. These equations represent the dielectric dispersion relation induced by ionic polarization. At neighbor of an arbitrary frequency ω' , the dielectric dispersion equation is approximately given by the parabolic equation,

$$\left. \frac{1}{k-1} \right|_{\omega' \sim \text{Neighbor}} = \frac{\omega_0^2}{C} \left[\left(\frac{4 \frac{\Gamma^2}{\omega_0^2}}{\left(1 - \frac{\omega'^2}{\omega_0^2}\right)^2} - 1 \right) \frac{\omega^2}{\omega_0^2} + \left(1 - \frac{4 \frac{\Gamma^2}{\omega_0^2} \cdot \left(\frac{\omega'^2}{\omega_0^2}\right)^2}{\left(1 - \frac{\omega'^2}{\omega_0^2}\right)^2} \right) \right], \quad [5]$$

especially at the infrared limit $\omega' / \omega_0 \rightarrow 0$, the dielectric dispersion relation becomes the simple parabolic equation as:

$$\left. \frac{1}{k-1} \right|_{\text{Infrared limit: } \omega' / \omega_0 \rightarrow 0} = \frac{\omega_0^2}{C} \left[\left(4 \frac{\Gamma^2}{\omega_0^2} - 1 \right) \frac{\omega^2}{\omega_0^2} + 1 \right]. \quad [6]$$

At the infrared limit, the damping coefficient Γ appears only in slope of ω^2 / ω_0^2 .

Figure 5 shows the $1/(k-1) - (\omega/2\pi)^2$ plot of the strained SrTiO₃ films. It was found that each curve was linear to ω^2 , and have a almost same y-intercept. The slope of the linear curves decreased as the tensile strain applied on SrTiO₃ films. These results show the dispersion relation at the infrared limit is proper approximation at the frequency region of 30 - 500 kHz. Based on the infrared-limit picture, invariable y-intercept showed that the tensile strain did not affect the eigenfrequency ω_0 of titanium-oxygen harmonic oscillation, and the decrease of the curve's slope showed that the strain affects the damping coefficient of titanium-oxygen ion dynamics. Figure 6 shows the damping coefficient as a function of tensile strain. It was found that as the tensile strain was applied to the SrTiO₃ film, the damping coefficient decreased. The reduction of the damping coefficient increased the electric dipole moment in the titanium-oxygen ionic oscillator, and the dielectric constant of the SrTiO₃ film was increased. From another point of view, the reduction of the damping coefficient was considered as a result of

Figure 5. $1/(k-1)$ -frequency relation: $1/(k-1)$ increased linearly as a function of $(\omega/2\pi)^2$.

Figure 6. Damping coefficient as a function of tensile strain. The damping coefficient was normalized by the eigenfrequency of ionic titanium-oxygen oscillator.

energy dissipation reduction; the energy dissipation via crystal lattice oscillation, in other word, phonon conduction decreased by applying the tensile strain.

Deep Tensile Strain and Dielectric Property

Figure 7 shows the increase of the dielectric constant induced by deep tensile strain. Up to the tensile strain of 0.025 %, at frequencies of 300 and 500 Hz, dielectric constants were increased linearly, and above the tensile strain of 0.025 %, increase of dielectric constant was saturated. This result showed the threshold of the strain-induced capacitance increase was situated near the tensile strain of 0.025 %.

Figure 7. Dielectric constant increase as a function of tensile strain.

Summary

The mechanically applied uniaxial strain on the SrTiO_3 MIM capacitor was investigated. The dielectric constant was enhanced by the uniaxial tensile strain, and at a frequency of 500 kHz, enhancement of 26.8 % was achieved. The effect of the tensile strain on SrTiO_3 ion dynamics was discussed. The tensile strain decreased the damping coefficient of titanium-oxygen ion oscillator. The reduction of the damping coefficient increased the electric dipole moment, and as a result, the dielectric constant of the SrTiO_3 film was increased. The threshold strain of the tensile strain-induce capacitance increase was 0.025 %. Under the threshold of 0.025 %, dielectric constant increased linearly, and above the threshold, dielectric constant was saturated. These results indicate the importance of strain design in fabrication process of high-k capacitors.

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