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Permittivity Enhancement of Mechanically Strained $SrTiO_3$ MIM Capacitor

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The possibility of strain engineering on $SrTiO_3$ high-k insulator was discussed. The tensile strain on $SrTiO_3$ 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 $SrTiO_3$ 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, $SrTiO_3$ and (Ba, Sr)TiO_3 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 $SrTiO_3$ thin film for a high performance RF MIM capacitor was also investigated [1].

Elastic strain-induced increase of dielectric constant on (Ba, Sr)TiO_3 film doped with Y (Yttrium) was reported [2]. Compressive strain in the (Ba, Sr)TiO_3 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)TiO_3 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 $SrTiO_3$ 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 $SrTiO_3$ thin film was deposited by metal-organic chemical vapor deposition (MOCVD) on a sputter-deposited Pt (200 nm) /TiOx (20 nm)/ SiO_2 (400 nm) / silicon substrate. The precursors of the $SrTiO_3$ 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 ethylcycrohexane. The $SrTiO_3$ film was deposited at a temperature of 525 ºC in a MOCVD reactor. The stoichiometry of the $SrTiO_3$ film was Sr/Ti = 50/50. The thickness of the $SrTiO_3$ film was 100 nm. Pt top electrode with a thickness of 180 nm was deposited on the top $SrTiO_3$ film using RF magnetron sputtering with a screen mask of 2 mm in diameter. Crystallinity of the $SrTiO_3$ film was measured by out-of-plane, and in-plane x-ray diffraction (XRD). Leakage current and dielectric properties of the $SrTiO_3$ 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 $SrTiO_3$ film were carried out.

In the capacitance-voltage measurement, the DC bias voltage V_{DC} on the $SrTiO_3$ 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 $SrTiO_3$ MIM capacitor was $V_{DC} + V_{osc}e^{i\omega t}$.

Characteristics of MOCVD $SrTiO_3$ thin films

The crystallinity of the $SrTiO_3$ 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 $SrTiO_3$ (200) at 2theta of 46.45 ° was observed, on the other hand, in the in-plane XRD spectrum, the peak of $SrTiO_3$ (110) at 2theta of 32.33 ° was dominantly observed. These results showed that the $SrTiO_3$ thin film had a crystallinity of (100) in the depth direction of the film, and also had a uniform crystallinity in the surface

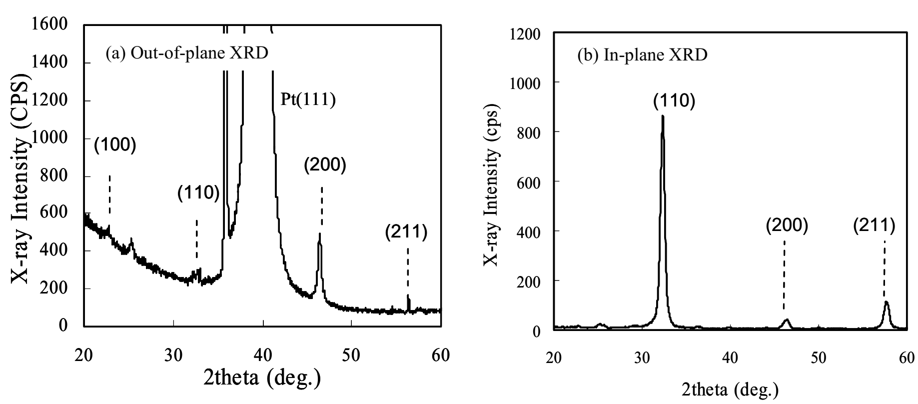

Figure 1. X-ray diffraction pattern of the $SrTiO_3$ thin films: (a) out-of-plane measurement and (b) in-plane measurement.

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 $SrTiO_3$ MIM capacitor was 1.51×10^{-6} and 2.77×10^{-6} A/cm^2 at bias electric fields of +0.10 and +0.20 MV/cm, respectively. This result showed that the MOCVD $SrTiO_3$ film had a good performance for DRAM high-k insulator.

Tensile Strain on $SrTiO_3$ MIM capacitor

Figure 2 shows a schematic diagram of the two-point bending method. The sample wafer with the $SrTiO_3$ film was installed on the bending apparatus and uniaxial tensile stress was mechanically applied, and the surface strain was produced on the $SrTiO_3$ film. Here the surface strain was estimated by the equation:

$$\varsigma = \left.\frac{\Delta L}{L}\right|_{\text{Surface}} \cong \frac{T\cdot\Delta y}{L^2}, \qquad [1]$$

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 ς 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 : $x_i \to x_i + u_i$.

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

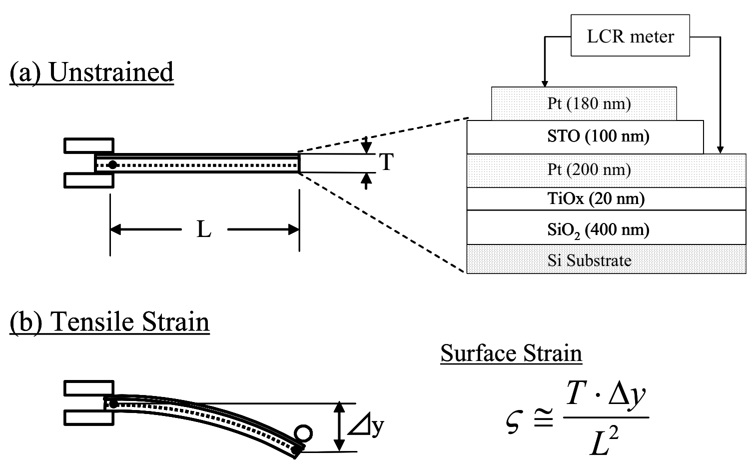

Figure 2. Schematic diagram of two-point bending method used for applying uniaxial tensile strain on the $SrTiO_3$ thin films.

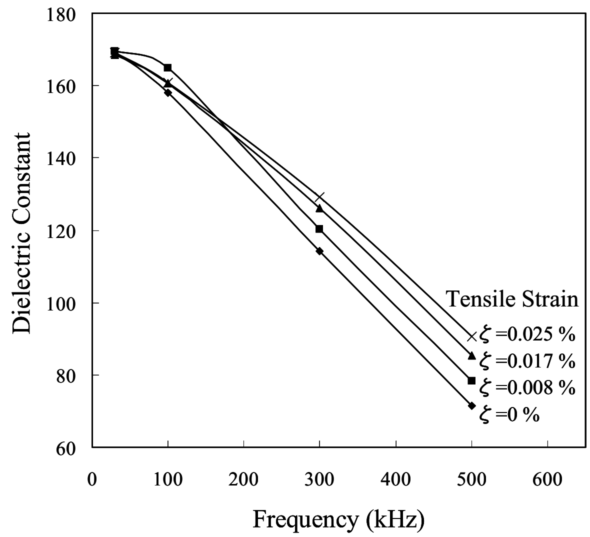

Figure 3. Tensile strain effect on dielectric constant of the $SrTiO_3$ thin films. After the tensile strain forced, the dielectric constant became larger.

appeared, and dielectric constant was increased. At a frequency of 500 kHz, the dielectric constant of the unstrained $SrTiO_3$ 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 $SrTiO_3$ 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 $SrTiO_3$, especially the relation between the strain and ion dynamics. In $SrTiO_3$ 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 $SrTiO_3$ 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:

$$M_{ion}\frac{d^2z}{dt^2}+2M_{ion}\Gamma\frac{dz}{dt}+M_{ion}{\omega_0}^2z=Z_{ion}eE_0\exp(i\omega t)\ , \qquad [2]$$

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 $P=Z_{ion}eN_{ion}z$ is obtained, and the dielectric constant is derived as

$$\varepsilon=1+\frac{e^2Z_{ion}^2N_{ion}}{\varepsilon_0M_{ion}}\frac{1}{({\omega_0}^2-\omega^2)+i2\Gamma\omega}\ , \qquad [3]$$

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

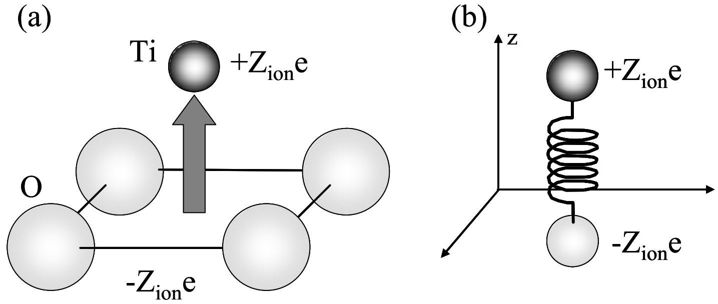

Figure 4. Schematic diagram of titanium-oxygen polarization in the $SrTiO_3$ thin films: (a) polarized titanium-oxygen configuration in the $SrTiO_3$ perovskite structure, and (b) the corresponding harmonic oscillator.

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

where k is the real part of the dielectric constant ε, and C is a constant coefficient $C=(e^2{Z_{ion}}^2N_{ion})/(\varepsilon_0 M_{ion})$. 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,

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

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

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

At the infrared limit, the damping coefficient Γ appears only in slope of $\omega^2/{\omega_0}^2$.

Figure 5 shows the $1/(k-1)$ - $(\omega/2\pi)^2$ plot of the strained $SrTiO_3$ 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 $SrTiO_3$ 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 $SrTiO_3$ 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 $SrTiO_3$ film was increased. From another point of view, the reduction of the damping coefficient was considered as a result of

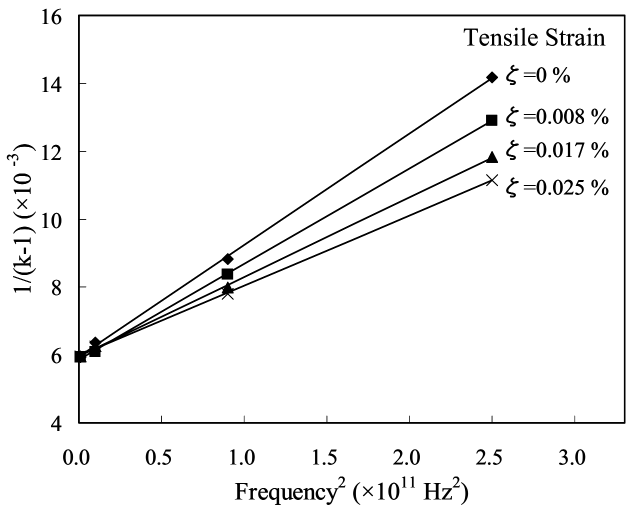

Figure 5. 1/(k-1)-frequency relation: 1/(k-1) increased linearly as a function of $(\omega/2\pi)^2$.

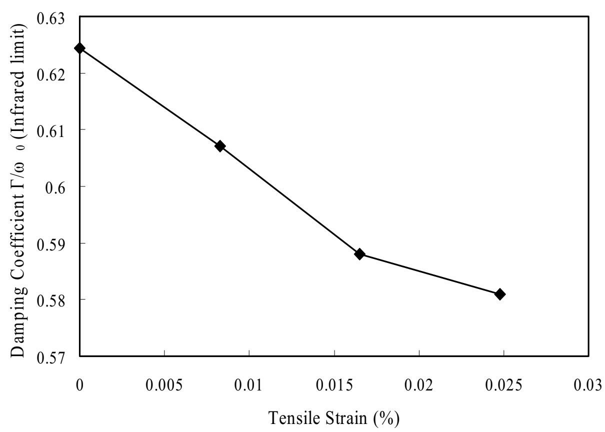

Figure 6. Damping coefficient as a function of tensile strain. The damping coefficient was normalized by the eigenfrequency of ionic titanium-oxygen oscillator.

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 %.

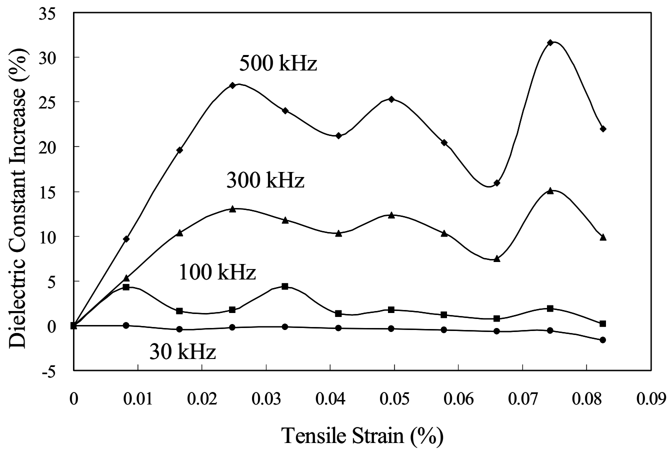

Figure 7. Dielectric constant increase as a function of tensile strain.

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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