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Increment of dielectric properties of SrTiO₃ thin films by SrO interlayer on Ru bottom electrodes

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SrTiO₃ thin films were deposited on Ru using plasma-enhanced atomic layer deposition with and without a SrO interlayer. When the SrTiO₃ films were deposited on Ru directly, the dielectric constants of the films decreased abruptly from 65 to 16 as the thickness fell below 20 nm. This change was related to film crystallinity. Conversely, when a seed layer was prepared by depositing 2.7 nm SrO and postannealing before SrTiO₃ deposition, the crystallinity of the SrTiO₃ films was enhanced and the thickness dependence of the dielectric constant was reduced. As a result, the dielectric constant of 10 nm SrTiO₃ films was improved from 16 to 50. © 2007 American Institute of Physics. [DOI: 10.1063/1.2768887]

As the size of the dynamic random access memory (DRAM) is scaled down, alternative oxide thin films with higher dielectric constants than typical SiO₂ or silicon oxide/nitride-based systems have received considerable attention for capacitor dielectrics. Of the various high-k materials investigated recently, strontium titanate (SrTiO₃) has attracted interest as a capacitor dielectric material in the next-generation DRAM with 1 Gbit density or higher. The attractive properties of SrTiO₃ thin films include a high dielectric constant (k ≈ 300) with a paraelectric phase in the normal range of operating temperatures, high breakdown strength, and good chemical stability. Since SrTiO₃ has such a high dielectric constant owing to the ionic polarization in its perovskite structure, the dielectric properties were critically dependent on the crystalline structure and stoichiometric composition. In general, as the thickness of the perovskite-structured oxide films decreases to a few tens of nanometers, the electric properties of the films deviate considerably from those of the bulk materials. In particular, the dielectric constant of the films decreases markedly with decreasing thickness owing to the small grain size of polycrystalline film. To improve the deviation of the electrical properties of perovskite-structured films from those of bulk, the use of a crystallization seed layer was introduced in the fields of superconducting electronics and ferroelectric materials. It has rarely been attempted for DRAM capacitor application because it is hard to fabricate the perovskite-structured seed layer on a noble metal electrode without loss of the dielectric properties. Among perovskite-related materials, strontium ruthenates (SRO) are conductive oxides that have a good lattice match with SrTiO₃. Therefore, ultrathin strontium ruthenate formed on the bottom electrode could be used as a crystallization seed layer, and the dielectric properties of SrTiO₃ thin films could be improved by enhancing the crystallinity. In this letter, we report about the dielectric properties in SrTiO₃ thin films, in the range of a few tens of nanometers, deposited using plasma-enhanced atomic layer deposition (PEALD), and the improved dielectric properties of SrTiO₃ films in the applicable thickness range of next-generation DRAM capacitors with the introduction of SRO as a crystallization seed layer.

SrTiO₃ thin films were deposited on 20 nm Ru/25 nm TiN/p-type Si wafers at a deposition temperature of 225 °C and a pressure of 3 Torr using PEALD adopting a supercycle concept for precise composition control. Sr(C₁₁H₁₉O₂)₂ and Ti(O₂–C₃H₇)₄ were used as precursors, and O₂ plasma was used as an oxidant. Sr(C₁₁H₁₉O₂)₂ was dissolved in butyl acetate (0.2 M) and supplied to the reaction chamber by a liquid delivery system. Ti(O₂–C₃H₇)₄ vapor was carried in argon gas at a flow rate of 50 sccm through a bubbler at 60 °C. The flow rates of the purge Ar and O₂ were 200 and 100 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. The thickness per cycle obtained from the converged regime was 0.036 nm/cycle for TiO₂ films and 0.054 nm/cycle for SrO films. One supercycle for deposition of stoichiometric SrTiO₃ consisted of six TiO₂ cycles and seven SrO cycles. The as-deposited films underwent rapid thermal annealing at 600 °C for 10 min under ambient N₂. To improve the dielectric properties of SrTiO₃ thin films, strontium ruthenate (SRO), a conductive oxide with a perovskite structure, was prepared as a crystallization seed layer on the Ru bottom electrode before SrTiO₃ deposition. In order to make the SRO seed layer, 2.7 nm of SrO were deposited on the Ru electrode and then annealed at 600 °C for 10 min under ambient N₂. X-ray diffraction (XRD) (Rigaku) analysis using Cu Kα radiation (λ = 1.5405 Å) was used to determine the crystal structures of the SrTiO₃ thin films. Cross-sectional transmission electron microscopy (TEM) was used to study the formation of the SRO interlayer, and the corresponding elemental information was determined using the energy dispersive x-ray spectrometry (EDS) TEM technique. To measure the dielectric constant, sputtered platinum was used as a top electrode and the dielectric constant was measured using a C-V analyzer (Keithley 590) at a frequency of 1 MHz.

The variation in the dielectric constant of SrTiO₃ thin films with film thickness is shown in Fig. 1(a). For the
SrTiO₃ films with thicknesses over 20 nm, the dielectric constant values were not as sensitive to the film thickness; however, with SrTiO₃ films with thicknesses less than 15 nm, the dielectric constants decreased dramatically with decreasing film thickness. In particular, the 10 nm SrTiO₃ film had a very low dielectric constant of 16, corresponding to an equivalent oxide thickness (EOT) of 2.5 nm. To investigate the dependency of the dielectric constant on SrTiO₃ film thickness, the crystallinity of the films was investigated using XRD analysis for film thicknesses in the range 10–30 nm.

As shown in Fig. 1(b), the 15 nm SrTiO₃ film had a lower peak intensity with a broad full width at half maximum compared to the SrTiO₃ films with thicknesses exceeding 20 nm. For the 10 nm film, no SrTiO₃ peak was observed. As such, it was thought that the reason SrTiO₃ thin films with thicknesses less than 15 nm had relatively low dielectric constants was related to film crystallinity.

To apply SrTiO₃ thin films as DRAM capacitor dielectrics under 65 nm technology, the dielectric constant of the STO thin films, with thicknesses under 15 nm, has to be increased. In order to improve the dielectric properties by enhancing the crystallinity of SrTiO₃ thin films, an ultrathin crystallization seed layer of SRO was prepared on the Ru bottom electrode before SrTiO₃ deposition. As shown in the cross-sectional TEM micrographs in Fig. 2(a), the deposited 2.7 nm SrO layer was crystallized after annealing in ambient N₂ at 600 °C; the EDS analysis of this crystallized layer is shown in Fig. 2(b). Although a quantitative compositional analysis could not be performed owing to the absence of a Sr–Ru–O standard sample, it was qualitatively observed that Sr and Ru elements coexisted in the crystallized layer. From these results, the ultrathin SrO layer was shown to have been transformed into a crystallized Sr–Ru–O compound by the postannealing process.

Figure 3 compares the XRD patterns of annealed 10, 15, and 20 nm SrTiO₃ thin films with and without a SRO layer on the Ru bottom electrodes. As a result of SRO insertion, the (100) and (200) peaks of the SrTiO₃ film disappeared, while the (110) peak intensity was increased. In particular, the (110) peak of the 15 nm SrTiO₃ thin film deposited on a SRO seed layer was increased markedly compared with that of the 15 nm SrTiO₃ thin film on Ru directly without SRO layer formation. For 10 nm SrTiO₃ films, the (110) peak of SrTiO₃ was detected for the sample deposited on a SRO seed layer even when no SrTiO₃ peak was observed for SrTiO₃ deposited on Ru directly.

After establishing the crystallinity enhancement of SrTiO₃ films by inserting a SRO seed layer, the dielectric properties of SrTiO₃ thin films after ambient N₂ annealing at 600 °C were investigated. The variation of dielectric properties of SrTiO₃ films is indicated in Table I. The dielectric constants of SrTiO₃ films deposited on a SRO seed layer were higher than for those deposited on Ru without a SRO layer, as indicated in Fig. 4. The dielectric constant of 10 nm SrTiO₃ films, which had very low dielectric constants without the seed layer owing to the lack of crystallinity, was increased to 50 by using the SRO seed layer. This increase was over three times that of the film formed on Ru directly without the SRO layer. Generally, the EOT of a dielectric
decreases linearly with decreasing film thickness. For very thin SrTiO$_3$ films on Ru, however, the EOT increased with decreasing film thickness, as indicated in Table I, due to the deviation of crystallinity from that of thicker films. With the insertion of the SRO seed layer, the EOT decreased with decreasing film thickness because the increment of the dielectric constant of thinner films was greater than that of thicker films and the EOT of 10 nm SrTiO$_3$ deposited on a seed layer was 0.8. According to these results, the SRO layer, formed by ultrathin SrO layer deposition and postannealing process between the SrTiO$_3$ thin film and the Ru bottom electrode, acted as a seed layer for crystallization of the SrTiO$_3$ films with thicknesses less than 15 nm. In summary, the dielectric constants of annealed SrTiO$_3$ films with thicknesses less than 15 nm decreased dramatically with decreasing film thickness due to poor crystallinity, whereas the dielectric constants were not as sensitive to the film thickness when thicker than 20 nm. As a result of inserting a SRO crystallinity-enhancing seed layer, formed by depositing a 2.7 nm SrO layer on the Ru bottom electrode and using a postannealing process, the dielectric constants of SrTiO$_3$ films were increased.

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<table>
<thead>
<tr>
<th>STO film thickness</th>
<th>10 nm</th>
<th>15 nm</th>
<th>20 nm</th>
<th>30 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without SRO layer</td>
<td>$\varepsilon_{\text{STO}}$</td>
<td>16</td>
<td>33</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>EOT</td>
<td>2.5 nm</td>
<td>1.8 nm</td>
<td>1.2 nm</td>
</tr>
<tr>
<td>With SRO layer</td>
<td>$\varepsilon_{\text{STO}}$</td>
<td>50</td>
<td>67</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>EOT</td>
<td>0.8 nm</td>
<td>0.9 nm</td>
<td>1.1 nm</td>
</tr>
</tbody>
</table>

FIG. 4. Dielectric constants of 10, 15, and 20 nm SrTiO$_3$ thin films with and without SRO seed-layer formation. (The SrTiO$_3$ thin films were annealed at 600 °C for 10 min in ambient N$_2$.)