Textured $SrTiO_3$ thin films on SiO_2/Si by liquid injection MOCVD using a new bimetallic precursor

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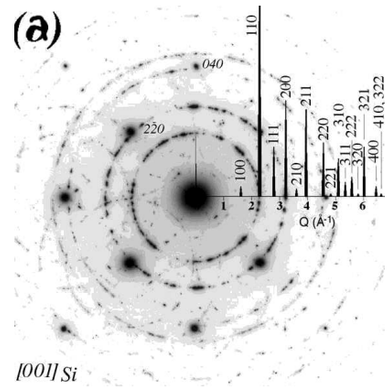
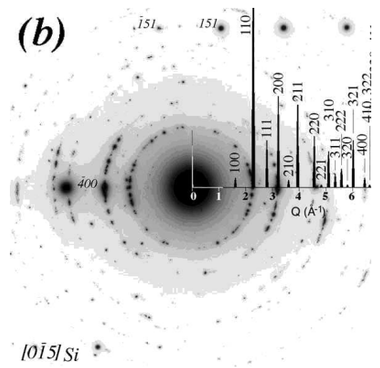
Technology roadmaps predict in near future the inadequacy of SiO_2 as gate oxide in the CMOS structures. $SrTiO_3$ is one of the most promising candidates due to its high bulk dielectric constant. Metalorganic Chemical Vapor Deposition (MOCVD) by injection allows a good coverage step. For this technique, the deposition of heteroxide thin films usually necessitates the use of two distinct precursors. As the properties of the two chemicals, such as volatility and reactivity in gas phase may differ, stoechiometry in the thin films has to be adjusted by accommodating the metallic ratio in solutions. A new bimetallic precursor – where the two metal species belong to the same molecule - was synthesized with the general formula $Sr_2Ti_2(thd)_4(OiPr)_8$ (1). We have studied the characteristics of thin films deposited on SiO_2/Si using this bimetallic precursor. The evolution of their properties as a function of chamber pressure and growth temperature was compared to $SrTiO_3$ thin films deposited under the same conditions but using the mixture of $Sr(thd)_2$ and $Ti(thd)_2(OiPr)_2$, that we will referred as the 'standard precursors'.
All the thin films grown under 2 to 9torr at 700°C and in the temperature range 550°C-800°C under either 2 or 5torr were found to be nearly stoechiometric, slightly deficient in strontium. These layers present other interesting properties. Under some pressure and temperature conditions, the thin films consist of highly $[001]_{Si}$ textured $SrTiO_3$. TEM observations of such a textured film are reported beside. For an orientation corresponding to the [001] zone axis of the Si substrate, the electron diffraction pattern on figure a exhibits reflection rings of the $SrTiO_3$ layer. The rings intensity for the *h00* and *hk0* are relatively intense compared to the $SrTiO_3$ polycristalline pattern. Some other reflections are even not observed. There is thus a unique [001] direction of $SrTiO_3$ crystals parallel to the $[001]_{Si}$ zone axis. A localization of intensity on *h00*, *hk0* rings in the 3D reciprocal space is confirmed from a slight tilt of the sample where parts of ring intensities remain around this rotation axis corresponding to the *h00* row of Si reflections (figure b).
Whatever the temperature is, the maximum effect of texturing is reported at the lowest pressure 2torr. Fixing pressure, there is a temperature range where the layers are textured. The maximum temperature interval for different pressures is more or less 50°C at 700°C under 2torr. We note that using the mixture of standard precursors this texturing effect does exist but is very weak. We would rather talk about a (001) crystallographic preferred orientation.
The bimetallic precursor has another advantage over the standard set of precursors. It allows obtaining carbonates-free and crystallized $SrTiO_3$ thin films at temperatures lower than 100°C than in the case of standard precursors.

We believe that this new bimetallic precursor is very attractive for future high-k dielectric applications.





Figures a and b: Electron diffraction patterns of a crystalline $SrTiO_3$ layer deposited under 2torr at 700 °C on a (001) Si substrate. Both diffraction patterns exhibit single reflections from the Si single crystal and rings from the $SrTiO_3$ layer. They are related by a rotation of 11.3 ° (angle between $[001]_{Si}$ and $[0\text{-}15]_{Si}$ zone axes) about the horizontal h00 row of Si reflections. Variations in $SrTiO_3$ reflection intensities observed through such a rotation are characteristic of a maximum of intensity for h00 and hk0 rings parallel to the $SrTiO_3$ / (001) Si interface plane.

(1) L.Hubert-Pfalzgraff, S. Daniele and co., *Journal of sol-gel Science and Technology*, **8**, 49-53,(1997)

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