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The Mg influence on the properties of $SrTiO_3$ thin films

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Abstract

The solid solubility limit of atomic substitutions is expected to be dependent on the size scale (bulk ceramics and films) of materials and on processing. In this work, the incorporation of Mg on A and B sites of $SrTiO_3$ (ST) thin films prepared by sol–gel on $Pt/TiO_2/SiO_2/Si$ substrates is investigated. The solid solubility of Mg evaluated by XRD analysis, is limited to $x \leq 30\%$ for A-site occupancy (SMT) and to $y \leq 40\%$ for B-site occupancy (STM). It is observed that the lattice constant decreases for SMT and increases for STM films with increasing concentration of Mg. The dielectric constant and loss tangent at room temperature are reduced for SMT and STM films. The losses of Mg-doped ST films are lower than 0.05. The tunability of doped ST films is about 6% at 100 kV/cm^2 and room temperature and its dependence on the Mg contents varies with dopant lattice site occupancy. The obtained behavior is compared with identical bulk ceramic compositions and discussed. The higher degree of chemical homogeneity attained in solution and the strains induced in the films are controlling parameters of the solid solubility of Mg on ST films.

Keywords: Films; Sol–gel processes; Impurities; Microstructure-final; Dielectric properties; $SrTiO_3$

1. Introduction

Strontium titanate (ST) based thin films have been recently investigated as suitable dielectric material for very large scale integrated devices, such as dynamic random access memories (DRAMs) and for tunable microwave applications (filters, phase shifters, resonant antennas), due to its high charge storage capacity, good insulating properties, high dielectric permittivity and low dielectric loss, field dependence of the dielectric permittivity, high break down strength and chemical stability. As an incipient ferroelectric ST retains its paraelectric behavior until almost 0 K. The dielectric constant increases to about 30,000 upon cooling and remains temperature independent below 3 K.[1] Owed to the quantum fluctuations of the atomic positions no paraelectric–ferroelectric anomaly is observed. However, it is well known that quantum fluctuations can be restrained by the application of high electric fields,[2] uniaxial stresses[3] or by atomic substitutions. Isovalent A-site substitutions in ST lattice with Ca,[4] Ba[5] and Pb[6] were reported to induce a low temperature ferroelectric-type anomaly, but no polar state was reported for Mg.[7,8] Recent studies[7,9] showed that the solid solubility of Mg in ST ceramics is limited, in opposition to the complete solid solution formation with the above-mentioned isovalent cations, Ba^{2+} and Pb^{2+}. Due to the ionic radius difference between Mg^{2+} and Sr^{2+} and proximity between Mg^{2+} and Ti^{4+}, the solubility of Mg ions is very limited (if any) at A sites, but *circa* 15% for B site.[7] Although predicted by Kvyatkovskii[10] no polar behavior in $SrTiO_3$ doped Mg ceramics was observed. Moreover, Mg B-site doping drives the system away from the ferroelectric instability.[7]

Considering that: (i) the absence of polar anomaly in Mg-doped ST ceramics, predicted by Kvyatkovskii, can be related to the absence of incorporation of Mg in the A site; (ii) chemical solution preparation processes allowing a higher degree of precursors homogeneity might favour a higher solid solubility in the lattice; (iii) for thin films the substrate effect can not be neglected and might affect the solid solubility limit of the dopant; (iv) the doping effect on ST materials has been mainly studied on single crystals and ceramics, not systematically on thin films and no data on dielectric properties Mg-doped ST films were reported until now, the Mg influence on the structure and dielectric properties of ST thin films prepared by

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sol–gel is under study. In this work, preliminary results on the structure, microstructure and low-frequency dielectric properties at room temperature are reported for $Sr_{1-x}Mg_xTiO_3$ and $SrTi_{1-y}Mg_yO_{3-\delta}$ thin films.

2. Experimental procedures

$SrTiO_3$, $Sr_{1-x}Mg_xTiO_3$ ($x = 0.01$, 0.05, 0.10, 0.20, 0.30, 0.40) (SMT) and $SrTi_{1-y}Mg_yO_{3-\delta}$ ($y = 0.01$, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50) (STM) solutions with a concentration of about 0.2 M were prepared using strontium acetate (98%, ABCR Germany), tetra-*n*-butyl orthotitanate (98%, MERCK, Germany) and magnesium acetate tetrahydrate (99.5%, MERCK, Germany) as starting precursors. Acetic acid (99.8%, MERCK, Germany), 1,2-propanediol (99.5%, Riedel-de Haën, Germany) and absolute ethanol (99.8%, MERCK, Germany) were used as solvents. Strontium acetate was initially dissolved into heated acetic acid ($T \sim 60\,^{\circ}C$) followed by the addition of magnesium acetate under constant stirring to form a transparent solution. After cooling to room temperature the former solution was diluted in 1,2-propanediol and titanium isopropoxide was added. The resultant clear solution was continuously stirred during 12 h in closed flask and ethanol was added as a final step. Using these solutions layers of SMT and STM were deposited on $Pt/TiO_2/SiO_2/Si$ substrate ($Pt \sim 150$ nm, $TiO_2 \sim 20$ nm, $SiO_2 \sim 300$ nm, $Si \sim 1$ mm) by dip-coating (substrate withdraw speed of 1.2 mm/s). Subsequently, the films were heated on a hot plate at 350 °C for 1 min. This step was repeated after each dipping to ensure complete removal of volatile species between each layer. After 10 layers, the films were annealed at 750 °C for 60 min. The film's crystalline structure was evaluated by XRD analysis (Rigaku D/Max-B, Cu Kα). The film's microstructure was examined by AFM (Multimode, Nanoscope IIIA, Digital Instruments) and SEM (Hitachi S-4100). Dielectric measurements were conducted on Metal Insulator Metal capacitors using Au as top and Pt as bottom electrodes. Dielectric permittivity and loss in the frequency range of 100 Hz–1 MHz, as well as the capacitance–voltage (*C*–*V*) curves were measured using a Precision LCR Meter HP 4284A at room temperature.

3. Results

Under the sol–gel procedure used in this work, clear and homogeneous precursor solutions were prepared for $Sr_{1-x}Mg_xTiO_3$ ($x = 0.01$, 0.05, 0.10, 0.20, 0.30) and $SrTi_{1-y}Mg_yO_{3-\delta}$ ($y = 0.01$, 0.05, 0.10, 0.20, 0.30, 0.40) compositions. Solutions prepared with higher Mg concentrations became opaque and with visible precipitates.

Fig. 1 shows the XRD patterns of ST, SMT and STM films annealed at 750 °C for 60 min. It can be seen that all films exhibit a cubic crystalline structure and are single perovskite phase with the exception of $y = 0.50$ STM. For $y = 0.50$ MgO phase is clearly observed. Thus, the solid solubility of MgO on ST films prepared by sol–gel and annealed at 750 °C is around 30% and 40% for A and B sites of the ST lattice, respectively. An earlier work of Suzuki et al.[11] reported also 30% solid solubility limit of Mg for $Sr_{1-x}Mg_xTiO_3$ films prepared by PLD on $SrTiO_3$ substrates. Much lower solid solubility was obtained for Mg-doped ceramics (<1% for SMT and <15% for STM).[7]

The values of the lattice constant a_0 calculated from XRD data for undoped and doped ST films are shown in Fig. 2. The lattice constant of undoped ST was found to be 3.9061 Å, which is in close agreement with the literature data for ST

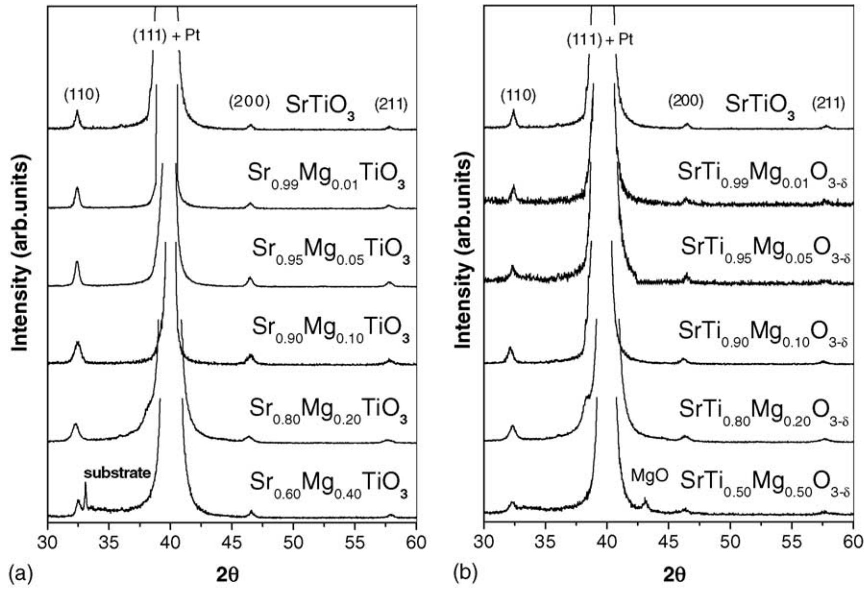

Fig. 1. X-ray diffraction patterns of the SMT (a) and STM (b) films annealed at 750 °C for 60 min.

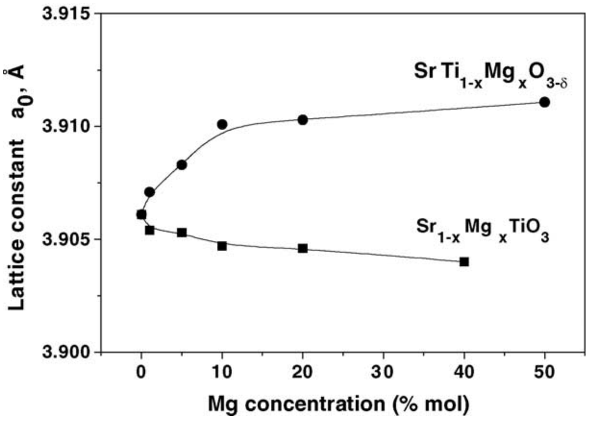

Fig. 2. Relationship between the lattice constant and Mg concentration in SMT and STM films.

ceramics[12]. The lattice constant slightly decreases for SMT and increases for STM films, markedly until 10%. This is reasonable taking into consideration the smaller (XIIcoord.) and bigger (VIcoord.) ionic radius of Mg^{2+} when substituting Sr^{2+} and Ti^{2+} ions, respectively. This evidently points to the introduction of Mg into either A or B sites of ST lattice of sol–gel thin films although clearly at B site. Similar increase of a_0 was observed for STM ceramics, however, a_0 variation for SMT ceramics was reported to be very small.[7]

Dense and crack free films were obtained with an average thickness of 350 nm (Fig. 3a). The increasing of Mg content in the films was confirmed by EDS (inset of Fig. 3a). No Mg rich regions were detected for the studied films. The surface morphology of Mg-doped ST films analyzed by AFM (Fig. 3b) shows that all films have a smooth surface with a roughness <2.3 nm.

The permittivity (ε_r) and loss tangent ($\tan\delta$) of ST, SMT and STM films measured at room temperature as a function of frequency are depicted in Fig. 4. The ε_r of undoped ST films presents a value of 250. Similar results were reported in the literature.[13] ε_r and $\tan\delta$ decrease as Mg content increases for both SMT and STM films (Fig. 4a). ε_r decreases as the frequency increases, being this variation more intense for undoped ST films (Fig. 4b). Similar results were reported for Mg-doped ST ceramics.[7]

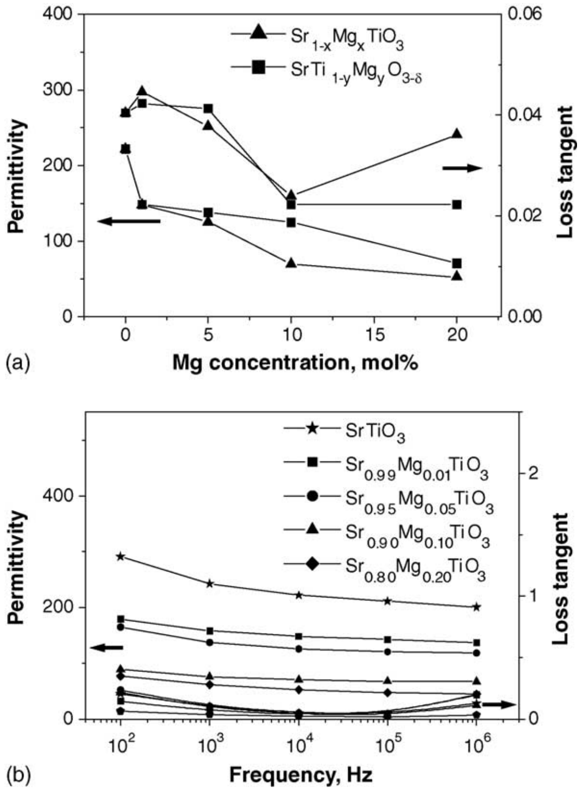

Fig. 4. Dielectric permittivity and loss tangent and of the SMT and STM films as function of concentration Mg dopant (at 100 kHz) (a) and dielectric permittivity and loss tangent of the SMT films as function of frequency (b).

The variation of ε_r versus electric field E was calculated from the measured results of capacitance versus dc-bias (C–V curves) and for SMT films is shown in Fig. 5. The capacitance of pure ST films is about 1.6 nF at $E = 0$ V, which is in close agreement with the literature data for ST[13] and is higher than the capacitance of doped ST films. As expected for a paraelectric behavior ε_r exhibits a small dependence on the applied voltage. ε_r (and capacitance, respectively) of SMT and STM films decreases with increasing Mg concentration and a similar variation with the applied voltage as ST is observed.

Tunability was calculated by the formula: tun (%) = $1 - \varepsilon(E)/\varepsilon(0) \times 100\%$, where $\varepsilon(0)$ is ε_r at zero bias and $\varepsilon(E)$

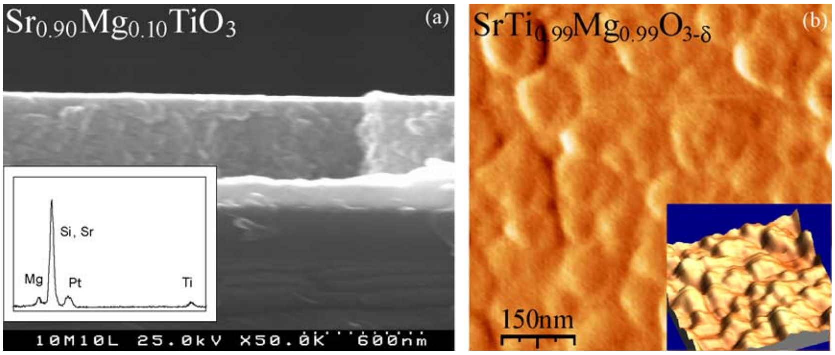

Fig. 3. Cross-section SEM images and EDS spectra (inset) of Sr$_{0.90}$Mg$_{0.10}$TiO$_3$ films (a) and atomic force micrographs of SrTi$_{0.99}$Mg$_{0.99}$O$_{3-\delta}$ films (b).

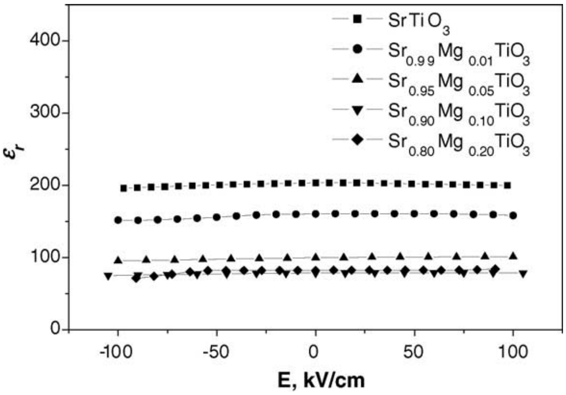

Fig. 5. The variation of ε_r from electric field E of the SMT films.

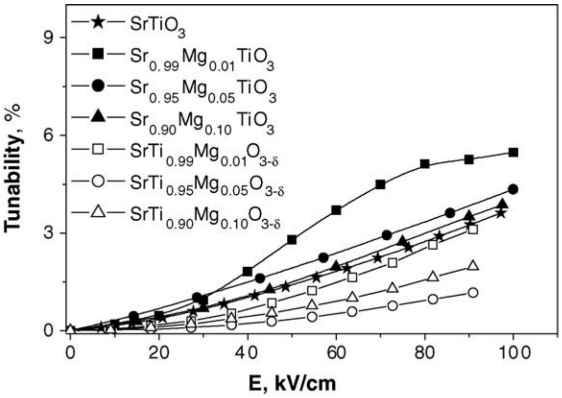

Fig. 6. Tunability of SMT and STM films.

is ε_r at the applied dc electric field. Fig. 6 exhibits the tenability–electric field variation for undoped and Mg-doped ST films at room temperature. The tunability of all the films does not exceed 6% at 100 kV/cm. As expected, the tunability of ST films at room temperature is not high, however, it increases for A-site Mg-doped films. The opposite effect is visible for B-site Mg-doped films. A different behavior was observed for Mg-doped ST ceramics, in which the tunability is less than 1% at room temperature, and decreases with the Mg content for both SMT and STM compositions.[7]

4. Discussion

Considering the ionic radius of $\mathrm{Sr}^{2+}_{(\mathrm{XII})}$ as 1.44 Å, of $\mathrm{Mg}^{2+}_{(\mathrm{XII})}$ as 1.21 Å (from the extrapolation using $\mathrm{Mg}^{2+}_{(\mathrm{VI})}$ and $\mathrm{Mg}^{2+}_{(\mathrm{VIII})}$ ionic radius values), of $\mathrm{Ti}^{4+}_{(\mathrm{VI})}$ as 0.605 Å and $\mathrm{Mg}^{2+}_{(\mathrm{VI})}$ as 0.72 Å, the difference between the ionic radius of Sr^{2+} and Mg^{2+} or Mg^{2+} and Ti^{4+} is more than 15% indicating a possible incorporation of Mg^{2+} in the ST lattice, according to Goldschmidt's rules.

The XRD and a_0 results presented above, confirm this indication and show that the solid solubility limit of Mg in ST lattice is higher for films than for ceramics, either for A (30% for SMT films and <1% for SMT ceramics[7]) or B site (40% for STM films and around 10% for STM ceramics[7]) of ST lattice. The higher degree of homogeneity at the molecular level attained in the sol–gel solutions used to prepare films, when compared with the mixed conventional oxide procedure, seems to be retained during the synthesis of the crystalline ST phase and a higher incorporation of Mg ions is allowed in the film's crystalline lattice. The chemical preparation of the precursors by itself can contribute to improve the solubility of Mg dopant, but similar results were reported for SMT films prepared by PLD.[11] Hence, other factors should be taken into account. It is well known also that due to different lattice constant (lattice mismatch) and different lattice thermal expansion coefficients between α, the film, and the underlying layers strains will be developed. As theoretically predicted Pertsev et al.[14] tensile strains induced in BST films by Pt/SiO$_2$ underlayers reduce the ε_r[15] and compressive strains induced in PZT films by the underlying electrode (SrRuO$_3$) and substrate improve the magnitude of the out of plane polarization of the ferroelectric film.[16] It is then plausible to expect that the mechanical strains induced in the film by the underlayers will also affect the solubility of the dopant.

The lattice mismatch between substrate and undoped and Mg-doped ST films can be calculated by: $(a_{\mathrm{substrate}}/a_{\mathrm{films}} - 1) \times 100\%$. The lattice constant for Pt (bottom electrode) is 3.912 Å and for Si is 5.403 Å. Lattice mismatch between film and Pt does not exceed 0.2%. Hence, Pt does not induce appreciable stresses on ST films. However, the lattice mismatch between film and Si substrate is higher, around 38%. Moreover, the thickness of Si layer is about 1 mm (three orders of magnitude higher than the film) and its thermal expansion coefficient plays a determinant role during the cooling process. Because α of ST is $9.4 \times 10^{-6}/C$ and of Si is $2.6 \times 10^{-6}/C$ during cooling tensile stresses will be developed. The existence of tensile strains will facilitate the incorporation of larger ions, such as Mg^{2+} in B site, and this might justify the results obtained in this work for STM films. The substrate can then be the reason for a higher incorporation of Mg in ST films lattice when compared with ceramics. On the other hand, the incorporation of smaller ions, such as Mg^{2+} in A site, might be facilitated by compressive strains. However, in this work also the incorporation of Mg into the A site of the ST lattice was observed. That indicates the possible existence of other mechanisms (such as point defects formation) that may account for the enhancement of the incorporation of Mg in A site for ST films. Further studies are required in order to clarify the solid solubility limits of dopants in ST films.

Since the solubility of Mg at A site of film's lattice is higher than in ceramics, it is then expected that the electric response of films will be somehow different. This was indeed observed in the present work for SMT compositions. The decrease of the dielectric permittivity in films is stepper than in ceramics and the tunability at room temperature increases for SMT films in opposition to the decrease observed in ceramics.[9]

The incorporation of Mg into A sites of ST lattice changes the intrinsic polarization of ST, changing the dielectric response and the field dependence, tunability. However, the observed effect deserves a detail investigation. Further studies on lattice vibration and dielectric response as a function of temperature and frequency, are now on going.

For STM films ε_r, tan δ and tunability decrease as Mg content increases. The observed variation is in accordance with the results observed for STM ceramics in which the fitting of the $\varepsilon_r(T)$ to Barrett's law indicates that Mg B-site doping drives the system away from the ferroelectric instability.[7] Similar decrease of the ε_r and tan δ with Mg was reported for BST films.[17] As in ceramics the decrease of the ε_r can be attributed to the lower polarizability of Mg ions together with the suppression of ferroelectric instability. For the case of films it should be also considered that, as predicted by Taylor et al.,[15] the existence of tensile strains will reduce ε_r. According to literature the loss tangent of ST single crystals[18] and ceramics[7] is lower than in films, and around 10^{-3}. In the present work, the losses of Mg-doped ST films are lower than 0.05 at 100 kHz and room temperature and exhibit a decrease with increasing of Mg concentration.

5. Conclusions

The solid solubility of Mg in ST thin films is limited and depends on the lattice site occupancy as observed for identical ceramic compositions. However, the solid solubility limit of Mg in ST films (A and B site) prepared by sol gel is higher, than in ST ceramics. Due to a high degree of homogeneity at the molecular level attained in the sol–gel precursor and to the thermal strains induced in the film by the underlayer Si substrate, a higher atomic substitution is tolerated in film's lattice structure. The lower polarizability of Mg ions and the tensile thermal stresses induced in the film can account for the observed decrease of ε_r and tan δ with increasing Mg content. On the other hand, the increase of tunability of SMT films at room temperature not observed in equivalent ceramic compositions points to the modification of ST lattice polarization.

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