

Determination of the stoichiometry and trace impurities in thin barium strontium titanate perovskite layers by inductively coupled plasma-mass spectrometry

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The determination of the stoichiometry in semiconducting and non-conducting thin layers is of importance for the study of growth mechanisms and for the control of defects during development and production. An analytical procedure using inductively coupled plasma-mass spectrometry (ICP-MS) was developed, employing different ICP-MS instruments [one double-focusing sector field ICP-MS (DF-ICP-MS) and two quadrupole ICP-MS without and with a hexapole collision cell (ICP-QMS and HEX-ICP-QMS, respectively)] for the determination of the stoichiometry and trace impurities in thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ perovskite films (BST) on silicon substrates after the dissolution of layers. The maximum sensitivity ($^{138}\text{Ba}^+$, 1720 MHz ppm⁻¹; $^{88}\text{Sr}^+$, 1330 MHz ppm⁻¹; $^{48}\text{Ti}^+$, 560 MHz ppm⁻¹), lowest detection limit (Ba, 0.004 ng l⁻¹; Sr, 0.007 ng l⁻¹; Ti, 0.08 ng l⁻¹) and best precision down to 0.11% relative standard deviation (RSD, at an analyte concentration of 1 µg l⁻¹) were achieved in DF-ICP-MS. HEX-ICP-QMS yielded a better sensitivity (HEX-ICP-QMS, 100–240 MHz ppm⁻¹; ICP-QMS, 23–50 MHz ppm⁻¹) and lower detection limit (HEX-ICP-QMS, 0.09–3.4 ng l⁻¹; ICP-QMS, 0.8–19 ng l⁻¹) in comparison with conventional ICP-QMS. Precision values of 0.3 and 0.2% RSD were observed for Ba/Sr and (Ba + Sr)/Ti ratios, respectively, by ICP-QMS and HEX-ICP-QMS at an analyte concentration of 10 µg l⁻¹. Besides ICP-MS, inductively coupled plasma-optical emission spectroscopy (ICP-OES) and X-ray fluorescence (XRF) analysis were used for the validation of the experimental results. The stoichiometric compositions measured by different methods are in good agreement taking into account the local inhomogeneity of element distribution in thin layers and the diffusion of elements in the substrate. Due to the high sensitivity of ICP-MS, the determination of 38 trace elements was performed in thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ films (with a thickness less than 60 nm) with detection limits in the low ng g⁻¹ range.

Introduction

Perovskite layers (such as superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ or non-conducting $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers) are of increasing importance for different applications in microelectronics. $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ is a prime candidate as a high-k dielectric in integrated high-density capacitors for future (multi-Gbit) DRAM memory cells.^{1,2} The most important defect of perovskite layers which needs to be controlled is deviation from the stoichiometric composition, because a change in stoichiometry can give rise to a change in the physical and chemical properties. Therefore, accurate and precise analytical techniques are required for stoichiometry control in deposited thin films.

A variety of techniques, including X-ray fluorescence (XRF) analysis,^{3–5} Rutherford backscattering spectroscopy (RBS),⁶ X-ray photoelectron spectroscopy (XPS),^{7,8} Auger electron spectroscopy (AES),⁸ transmission and scanning electron microscopy (TEM and SEM)^{3,8} and inductively coupled plasma-optical emission spectroscopy (ICP-OES) after chemical digestion,⁹ have been applied for the determination of stoichiometry in thin layers, layered systems and bulk materials. Solid state analytical methods are preferable for the direct determination of stoichiometry because they do not require sample pretreatment. For example, the change in the stoichiometry by laser pulsed vapour deposition and the effect of trace elements on the properties of high-superconducting thin layers with a perovskite structure were studied by XRF, SEM, RBS, proton-induced X-ray emission (PIXE) and laser

ionization mass spectrometry (LIMS) by Dietze and co-workers.^{4,6,10,11}

The stoichiometry of thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ (BST) perovskite layers, which were prepared by metal organic chemical vapour deposition (MOCVD) on silicon substrates with different buffer layers (*e.g.* Pt/ZrO₂/SiO₂), has been routinely measured using XRF at the Research Centre Jülich.^{12,13} The precision of the stoichiometric determination of thin BST layers (thickness, ~60 nm) was 0.4–1%. In particular, the accuracy of the Ti determination in thin BST layers using XRF can be insufficient if Ti diffuses into the buffer layers, because the penetration depth of the X-ray beam is too large to distinguish Ti in different layers. XRF is often not sufficiently sensitive for stoichiometry measurement in solid films with a lower thickness.

Therefore, highly sensitive analytical methods for the validation of XRF results are required for the determination of the stoichiometry in thin BST layers with high precision and accuracy. Inorganic mass spectrometry, especially inductively coupled plasma-mass spectrometry (ICP-MS), has been successfully used for simultaneous multielement determination at different concentration levels (for the determination of major and minor elements, trace and ultratrace impurities).¹⁴ At present, only a few papers have focused on the determination of stoichiometry in thin layers, and the possible influence of trace impurities on the electrical properties of $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ perovskite layers is unknown.

The aims of this paper were to develop an analytical method

for the determination of the stoichiometry and trace impurities in $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers and to compare the capability of different ICP-MS instruments.

Experimental

Instrumentation

Two quadrupole-based ICP-MS (ICP-QMS) [ELAN 6000 (Perkin Elmer Sciex, Ontario, Canada) and Platform (Micromass Ltd., Manchester, UK)] and a double-focusing sector field ICP-MS (DF-ICP-MS) [ELEMENT (Finnigan MAT)] were employed to determine the stoichiometry and trace impurities in thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers. The ICP-MS Platform was equipped with a hexapole collision cell (HEX-ICP-QMS) filled with helium and hydrogen. All ICP-MS measurements were carried out at low mass resolution ($m/\Delta m = 300$). Microconcentric MicroMist nebulizers (Model MicroMist AR30-1F02), with solution uptake rates of $320 \mu\text{l min}^{-1}$, attached to a minicyclonic spray chamber (both from Glass Expansion, Pty Ltd., Camberwell, Victoria, Australia), were used for solution introduction into the inductively coupled plasma. Solution aspiration was performed with a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany). The experimental parameters are summarized in Table 1.

An IRIS Advantage ICP-OES (TJA Solutions, Cheshire, UK) was used for comparative measurements of the concentration of Ba (via spectral lines of 233.5, 455.4 and 493.4 nm), Sr (407.7 and 421.5 nm) and Ti (323.4, 336.1 and 368.5 nm) in dissolved films. An X-ray fluorescence spectrometer, RIGAKU S/MAX (RIGAKU Corp., Osaka, Japan; RH anode, beam diameter of 30 mm, equipped with a scintillation detector for the registration of hard X-ray fluorescence radiation by Ti to U and a proportional counter for the registration of soft X-ray fluorescence radiation by Na to Ti), was applied for the direct non-destructive measurement of the stoichiometry in thin films. The instrument applied is capable of routinely measuring concentrations of the matrix elements Ba, Sr and Ti in thin perovskite layers with a precision of better than 1%. The X-ray fluorescence spectrometer was calibrated using standard layers prepared by chemical solution deposition with known concentrations of analytes; the standard matrix corresponding to the matrix of the sample perovskite layers.

Samples and reagents

Samples consisted of thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers (film thickness, 14–75 nm) on Si substrates with SiO_2 , IrO_2 and/or Pt buffer layers. The samples were obtained by MOCVD in a multiwafer planetary reactor.¹³ For quality assurance, a reference sample prepared by chemical solution deposition was used. The composition of the reference layer was determined exactly using known element weights for the preparation.

Single and multielement standard stock solutions for the calibration procedures were obtained from Merck (Darmstadt, Germany). For all dilutions, deionized Milli-Q water (18 M Ω) from a Millipore Milli-Q-Plus water purifier and sub-boiled nitric acid were used.

Sample preparation

The thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ films on Si substrates with buffer layers were divided into four parts. The layers were dissolved quantitatively with 0.1 ml of a mixture consisting of concentrated sub-boiled HNO_3 , HF (analytical grade purity) and Milli-Q water (1 : 2 : 10). If the solution contained an undissolved residue of the removed layer, it was boiled with the addition of the acid mixture until complete dissolution of the remaining layer. The solution obtained was diluted to 10 ml with Milli-Q water. The completeness of dissolution was controlled by depth profiling of Ba, Sr and Ti on the substrate with secondary ion mass spectrometry (SIMS, CAMECA ims 4f). For the ICP-MS measurements, the samples and blank acid mixture were further diluted from 1 : 10 to 1 : 50 depending on the analyte concentration in the original samples and acidified with 2% sub-boiled HNO_3 . For the measurement of stoichiometry with ICP-OES, dissolved and diluted 10 ml samples were studied. The thin films were measured directly by XRF without sample preparation.

Measurement procedure

The experimental parameters for the measurement of the stoichiometry and trace impurities by ICP-MS were optimized with respect to the maximum ion intensity of $^{138}\text{Ba}^+$, $^{88}\text{Sr}^+$ and $^{48}\text{Ti}^+$ as well as good precision for Ba/Sr and (Ba + Sr)/Ti atomic ratios.

The Ba/Sr and (Ba + Sr)/Ti atomic ratios of the metallic component of the $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ films were determined by ICP-MS using $^{137}\text{Ba}^+$, $^{138}\text{Ba}^+$, $^{86}\text{Sr}^+$, $^{88}\text{Sr}^+$, $^{48}\text{Ti}^+$ and $^{49}\text{Ti}^+$ as analyte ions. Three diluted samples were prepared from each original sample ($N = 3$) and the number of measurements was five ($n = 5$).

Furthermore, trace elements in thin dissolved BST layers were determined by ICP-MS (using ELAN 6000) using an external calibration with standard solutions of 38 analytes. $10 \mu\text{g l}^{-1}$ of ^{103}Rh was added to all solutions as an internal standard element for quantitative ICP-MS measurements. The regression coefficients for the calibration curves were better than 0.999.

Results

Optimization of ICP-QMS

The results of optimization of ELAN 6000 ICP-MS, in order to achieve maximum ion intensity for $^{138}\text{Ba}^+$, $^{88}\text{Sr}^+$ and $^{48}\text{Ti}^+$ as

Table 1 Experimental parameters for the determination of stoichiometry in thin perovskite layers by two ICP-QMS (with and without collision cell) and DF-ICP-MS

	ICP-QMS ELAN 6000 (PE Sciex)	HEX-ICP-QMS Platform (Micromass)	DF-ICP-MS ELEMENT (Finnigan MAT)
Nebulizer type	MicroMist	MicroMist	MicroMist
Spray chamber	Minicyclonic	Minicyclonic	Minicyclonic
Solution uptake rate/ml min ⁻¹	0.32	0.3	0.2
Rf power/W	1350	1350	1090
Coolant gas flow rate/l min ⁻¹	13.5	13.5	14
Auxiliary gas flow rate/l min ⁻¹	0.7	1.0	0.8
Nebulizer gas flow rate/l min ⁻¹	0.86	0.88	0.96
Helium flow rate/ml min ⁻¹		8.0	
Hydrogen flow rate/ml min ⁻¹		2.0	
Scanning mode	Peak hopping	Peak hopping	Peak hopping
Detection system dead time/ns	53	—	27
Mass resolution $m/\Delta m$	300	300	300

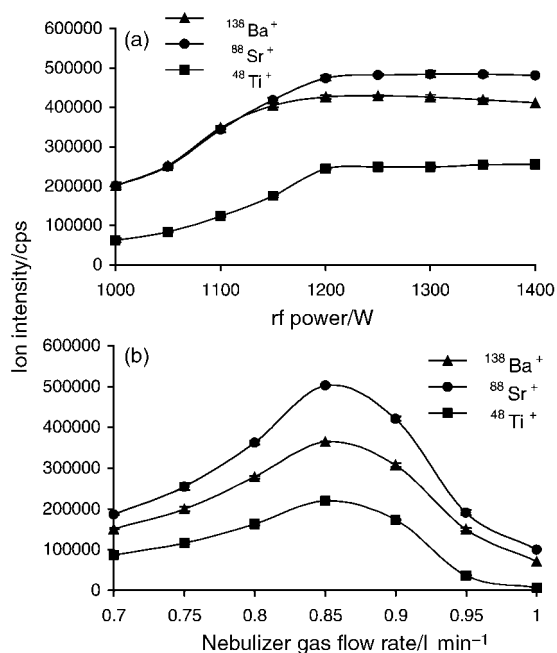


Fig. 1 Dependence of ion intensity of $^{138}\text{Ba}^+$, $^{88}\text{Sr}^+$ and $^{48}\text{Ti}^+$ on rf power at a nebulizer gas flow rate of 0.86 l min^{-1} (a) and on nebulizer gas flow rate at an rf power of 1350 W (b).

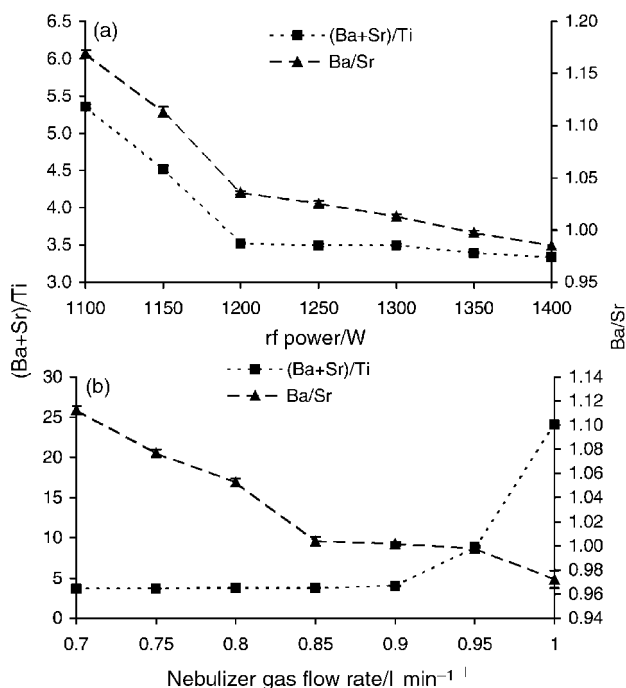


Fig. 2 Dependence of the measured atomic ratios $(\text{Ba} + \text{Sr})/\text{Ti}$ and Ba/Sr on rf power (a) and on nebulizer gas flow rate (b) in a Ba, Sr and Ti solution ($10\text{ }\mu\text{g l}^{-1}$ of each).

well as good precision for Ba/Sr and $(\text{Ba} + \text{Sr})/\text{Ti}$ atomic ratios with respect to the experimental parameters (rf power and nebulizer gas flow), using a $10\text{ }\mu\text{g l}^{-1}$ solution of Ba, Sr and Ti

Table 3 Precision (%) for Ba, Sr, Ti and their ratios measured by DF-ICP-MS ($1\text{ }\mu\text{g l}^{-1}$) and by ICP-QMS and HEX-ICP-QMS ($10\text{ }\mu\text{g l}^{-1}$)

Element	DF-ICP-MS Precision ($n = 6$) (%)	ICP-QMS	HEX-ICP-QMS
Ba	0.11	1.2	0.9
Sr	0.12	1.0	1.3
Ti	0.14	1.3	1.2
Atomic ratio			
Ba/Sr	0.17	0.34	0.30
$(\text{Ba} + \text{Sr})/\text{Ti}$	0.20	0.23	0.24

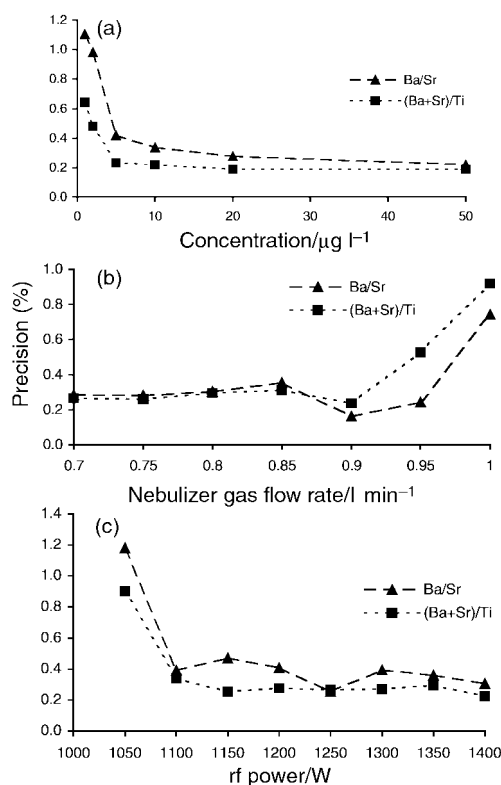


Fig. 3 Precision of atomic ratio measurement as a function of element concentration (a), nebulizer gas flow rate (b) and rf power (c) ($n = 10$).

in 2% nitric acid, are shown in Figs. 1–3. The maximum ion intensities for $^{138}\text{Ba}^+$, $^{88}\text{Sr}^+$ and $^{48}\text{Ti}^+$ were obtained at an rf power of ICP of 1350 W and a nebulizer gas flow rate of 0.86 l min^{-1} (Fig. 1). The same optimization procedure was performed for HEX-ICP-MS (Platform) and DF-ICP-MS (ELEMENT). The sensitivities (in MHz ppm^{-1}) and limits of detection (LOD, in ng l^{-1} , 3σ criterion) obtained for Ba, Sr and Ti with different ICP-MS methods are compared in Table 2. The highest sensitivity observed in DF-ICP-MS for Ba, Sr and Ti varied in the range $900\text{--}1800\text{ MHz ppm}^{-1}$. HEX-ICP-QMS yielded a better sensitivity and a better detection limit by up to ten times in comparison with conventional ICP-QMS. In Fig. 2, the dependence of the atomic ratios $(\text{Ba} + \text{Sr})/\text{Ti}$ and

Table 2 Sensitivities (MHz ppm^{-1}) and limits of detection (LOD) (ng l^{-1}) obtained with different ICP-MS instruments for Ba, Sr and Ti

Element	DF-ICP-MS		ICP-QMS		HEX-ICP-QMS	
	Sensitivity/ MHz ppm^{-1}	LOD/ ng l^{-1}	Sensitivity/ MHz ppm^{-1}	LOD/ ng l^{-1}	Sensitivity/ MHz ppm^{-1}	LOD/ ng l^{-1}
Ba	1720	0.004	37	0.8	244	0.09
Sr	1330	0.007	50	19	242	3.4
Ti	560	0.08	23	8.3	100	1.3

Table 4 Results of determination of stoichiometry in $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layer using different instruments and methods (average concentration $\pm 2\sigma$)

Atomic ratio	DF-ICP-MS (ELEMENT)	HEX-ICP-QMS (Platform)	ICP-QMS (ELAN-6000)	ICP-MS average
Ba/Sr	1.67 ± 0.02	1.71 ± 0.02	1.67 ± 0.02	1.68 ± 0.04
(Ba + Sr)/Ti	0.86 ± 0.02	0.86 ± 0.01	0.86 ± 0.02	0.86 ± 0.01

Table 5 Stoichiometry (atomic ratios) of Ba, Sr and Ti measured in three parts of the same sample (average concentration $\pm 2\sigma$)

Atomic ratio	I	II	III
Ba/Sr	1.94 ± 0.03	2.02 ± 0.03	1.96 ± 0.03
(Ba + Sr)/Ti	0.84 ± 0.02	0.98 ± 0.02	0.92 ± 0.02

Table 6 Concentrations (mg l^{-1}) of Ba, Sr and Ti measured in two dissolved $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers with ICP-QMS and ICP-OES

Sample Method Element	A		B	
	ICP-QMS	ICP-OES	ICP-QMS	ICP-OES
	Concentration/ mg l^{-1}			
Ba	86.6 ± 0.8	85.2 ± 2.6	64.8 ± 0.9	61.2 ± 3.2
Sr	25.8 ± 0.4	26.4 ± 1.6	26.3 ± 0.4	28.0 ± 1.5
Ti	44.4 ± 0.8	47.7 ± 3.6	127.2 ± 3.2	—

Ba/Sr on the rf power and nebulizer gas flow rate is shown using ELAN 6000 ICP-QMS. The curves in Fig. 2 show a change in the measured atomic ratio as a function of the investigated experimental parameters, which is due to the different ionization potentials of Ba, Sr and Ti (Ba, 5.21 eV; Sr, 5.69 eV; Ti, 6.82 eV). Thus, at lower rf power and higher nebulizer gas flow rate, the degree of ionization of Ti is lower in comparison with that of Ba and Sr, leading to an increase in the measured (Ba + Sr)/Ti ratio. Therefore, optimized parameters (Table 1) were chosen in the plateau range in order to minimize the influence of the possible deviation of rf power and nebulizer gas flow rate during the measurement on the measured ratio, as well as to achieve an accurate atomic ratio and a good precision and sensitivity. The precision of the $^{138}\text{Ba}^+$, $^{88}\text{Sr}^+$ and $^{48}\text{Ti}^+$ ion intensities and the Ba/Sr and (Ba + Sr)/Ti atomic ratios using different ICP-MS is compared in Table 3. The measurement of Ba^+ , Sr^+ and Ti^+ ion intensities using DF-ICP-MS yielded the best precision down to 0.11% (RSD). For Ba/Sr and (Ba + Sr)/Ti ratios ($n = 10$), precisions of 0.17 and 0.12% (RSD), respectively, were achieved when analysing an aqueous solution with an element concentration of $1 \mu\text{g l}^{-1}$.

The dependence of the measurement precision of the Ba/Sr and (Ba + Sr)/Ti ratios on the analyte concentration, nebulizer gas flow rate and rf power is shown in Fig. 3 using ELAN 6000 ICP-QMS. At an analyte concentration of $10 \mu\text{g l}^{-1}$ (acidified to 2% nitric acid), precisions of 0.34 and 0.23% (RSD) were achieved for Ba/Sr and (Ba + Sr)/Ti ratios ($n = 10$), respectively, by ICP-QMS, and 0.30 and 0.24%, respectively, by HEX-ICP-QMS. However, the precision was relatively low (about 1% for the Ba/Sr ratio and about 0.3% for the (Ba + Sr)/Ti ratio at $n = 5$) in the case of real dissolved thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers due

to higher blank values, possible contamination and increased molecular ion formation [using an acid mixture ($\text{HNO}_3 + \text{HF}$) to digest the BST layers].

Determination of the stoichiometry of thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers

At the initial experimental stage, element contents were analysed in samples with a non-stoichiometric composition, which were produced under different conditions during the development of the thin film deposition procedure. An example of stoichiometry determination in a $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ film with different ICP-MS instruments is given in Table 4. The experimental results obtained with DF-ICP-MS, ICP-QMS and HEX-ICP-QMS coincide within experimental error. However, the analytical results may be affected by the possible non-homogeneity of the investigated samples. The atomic ratios may differ from part to part because of local defects in stoichiometry (non-uniform distribution of the elements). In Table 5, the measurement results are presented for different parts of the same sample. The variation of the measured Ba/Sr ratio was within 3%, while the variation of the (Ba + Sr)/Ti ratio reached up to 15% at this experimental stage.

A comparison of Ba, Sr and Ti concentrations measured in dissolved samples using ICP-MS and ICP-OES is presented in Table 6. The results for Ba and Sr agree within experimental errors. However, the concentrations of Ti in the analysed samples were near the detection limit of ICP-OES and therefore are less accurate.

The results of stoichiometry determination using ICP-MS and XRF are compared in Table 7 for a $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ thin layer with ideal stoichiometry prepared by wet deposition ('reference' sample) as well as for a BST layer with nearly 'ideal' stoichiometry prepared by MOCVD. Only a small part of the latter sample was available for ICP-MS analysis; furthermore, this layer was chemically resistant, and therefore the acid concentration in the solution was increased in order to dissolve it completely. This caused more hard matrix effects in comparison with the previous measurement (Table 4), and hence a larger relative standard deviation of the ICP-MS results was observed. In general, the average results of ICP-MS and XRF are in good agreement taking into account experimental errors as well as the inhomogeneity of the analysed samples. The inhomogeneity of element distribution (determination of lateral distribution of matrix elements and depth profiling) in thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers was studied using sputtered neutral mass spectrometry (SNMS).^{12,15}

In Table 8, the contents of trace impurities measured in two $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ dissolved samples (original sample quantity, 100 μl) are presented, together with the LODs. The LODs in thin films were determined from the mass spectrum of the (matrix-matched) blank solution using the 3σ criterion (the LOD is given by $m_b + 3\sigma_b$, where m_b is the mean value of the

Table 7 Atomic ratios Ba/Sr and (Ba + Sr)/Ti in dissolved $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers measured with ICP-MS and XRF

Atomic ratio	1 ^a		2 ^b		Ideal stoichiometry
	ICP-QMS	XRF	ICP-MS (average)	XRF	
Ba/Sr	2.28 ± 0.02	2.27 ± 0.02	2.38 ± 0.15	2.34 ± 0.02	2.33
(Ba + Sr)/Ti	0.98 ± 0.01	1.00 ± 0.02	1.01 ± 0.03	1.00 ± 0.02	1.00

^a1: $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layer with ideal stoichiometry prepared by wet deposition ('reference' sample). ^b2: $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layer with nearly 'ideal' stoichiometry prepared by MOCVD.

Table 8 Limits of detection (LOD/ $\mu\text{g l}^{-1}$) of ICP-QMS (ELAN 6000) for trace elements calculated in diluted samples (initial sample quantity, 100 μl ; dilution factor, 1000) and content of trace elements (ng) in two perovskite layers

Element	LOD/ $\mu\text{g l}^{-1}$	Element content/ng		Element	LOD/ $\mu\text{g l}^{-1}$	Element content/ng	
		I	II			I	II
Ag	0.04	5.6±0.4	<4	Mn	0.002	29.7±2.7	2.1±0.2
Cd	0.006	3.8±0.1	32.2±0.7	Mo	0.3	<30	<30
Ce	0.0013	13.5±2.4	0.34±0.04	Nd	0.002	4.9±0.1	<0.2
Co	0.003	1.7±0.2	0.30±0.09	Pb	0.004	48.4±0.6	5.6±0.2
Cr	0.02	7.2±1.3	<2	Pd	0.02	43.7±1.6	<2
Cu	0.04	29±1	10.5±0.6	Pr	0.002	1.4±0.3	<0.2
Dy	0.002	1.6±0.4	<0.2	Pt	0.002	0.28±0.07	<0.2
Er	0.002	0.8±0.2	<0.2	Rb	0.014	4.8±0.4	1.6±0.2
Eu	0.002	1.2±0.1	0.80±0.05	Sb	0.004	4.1±0.2	<0.4
Fe	0.02	884±22	132±17	Se	0.013	18±2	18±4
Ga	0.002	54±5	36±1	Sm	0.002	4.4±0.1	2.8±0.1
Gd	0.003	1.7±0.3	<0.3	Th	0.02	3.5±0.2	<2
Ge	0.02	12±7	<2	Tm	0.003	1.3±0.2	<0.3
Hf	0.08	15±0.5	<8	U	0.003	1.7±0.1	0.29±0.04
Ho	0.002	0.22±0.04	<2	V	0.08	12.8±0.3	<8
La	0.0015	5.1±1.0	0.17±0.04	Y	0.002	6.2±1.2	0.96±0.10
Li	0.016	78±8	44±4	Yb	0.002	0.87±0.20	<0.2
Lu	0.0015	0.34±0.10	<0.15	Zn	0.004	420±8	613±19
Mg	0.4	818±34	135±28	Zr	0.2	650±10	25±4

blank measurements and σ_b is the standard deviation of five independent measurements of the blank value) considering the measured ion intensities in multielement standard solutions with known element concentrations. These LODs were affected by the blank values of ICP-MS and chemicals and the disturbing interferences of molecular ions on the atomic ions of the analyte. The measured trace element concentrations differed from sample to sample (see Table 8) depending on the chemicals and experimental conditions used for $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layer deposition. Furthermore, contamination with trace impurities during layer preparation was detected.

Conclusions

The high sensitivity of ICP-MS achieved at small solution uptake rates allows the determination of major and trace elements in thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ films after their dissolution. The analytical results of ICP-QMS were verified by comparison with independent analytical methods, such as ICP-OES and XRF. In general, a comparison of the different analytical methods yielded good agreement between the applied techniques. However, some differences in the obtained results were observed, because non-destructive XRF refers to the whole analyte quantity, including that part of the analyte diffused in the substrate, whilst ICP-QMS only refers to the dissolved surface film. The study of these effects, including $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layer profiling using other methods such as secondary ion mass spectrometry and X-ray-induced photoelectron spectroscopy, together with ICP-MS and XRF, will be the subject of forthcoming work. Of the applied analytical techniques, only ICP-MS allowed the analysis of trace impurities in $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ samples, which is important for the control of deposition processes and defects in thin $\text{Ba}_x\text{Sr}_y\text{TiO}_3$ layers.

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References

- 1 A. I. Kington, S. K. Streiffer, C. Basceri and S. R. Summerfelt, *MRS Bull.*, 1996, **21**(7), 46.
- 2 S. Yamamichi, H. Yabuta, T. Sakuma and Y. Miyasaka, *Appl. Phys. Lett.*, 1994, **64**, 1664.
- 3 H. J. Kwon, W. Jo, H. H. Kim, Y. W. Jeong, J. S. Lee, H. R. Yoon, I. S. Ban and J. R. Bogert, *J. Korean Phys. Soc.*, 1998, **32**, S1559.
- 4 J. S. Becker and H.-J. Dietze, *Physica C*, 1990, **167**, 509.
- 5 P. C. Van Buskirk, J. F. Roeder and S. Bilodeau, *Integrated Ferroelectrics*, 1995, **10**, 9.
- 6 M. Lorenz, J. S. Becker, H.-J. Dietze, W. Schmitz, B. Brunner and K. F. Renk, *Physica C*, 1991, **182**, 114.
- 7 C. J. Lu, A. X. Kuang and G. Y. Huang, *J. Appl. Phys.*, 1996, **80**, 202.
- 8 Y. Gao, S. He, P. Alluri, M. Engelhard, A. S. Lea, J. Finder, B. Melnick and R. L. Hance, *J. Appl. Phys.*, 2000, **87**, 124.
- 9 R. Kucharkowski, C. Vogt and D. Marquardt, *Fresenius' J. Anal. Chem.*, 2000, **366**, 146.
- 10 J. S. Becker, M. Lorenz and H.-J. Dietze, *Proceedings of SPIE's Technical Symposium on Microelectronics, Processing, Integration '91*, San Jose, September 9–13, 1991.
- 11 M. Lorenz, H.-K. Bothe, J. S. Becker and H.-J. Dietze, *Fresenius' J. Anal. Chem.*, 1991, **341**, 114.
- 12 J. S. Becker and S. Boulyga, *Fresenius' J. Anal. Chem.*, in the press.
- 13 P. Ehrhart, F. Fitsilis, S. Regnery, R. Waser, F. Schienle, M. Schumacher, M. Dauelsberg, P. Strzyzewski and H. Juergensen, *Integrated Ferroelectrics*, in the press.
- 14 J. S. Becker and H.-J. Dietze, *Int. J. Mass Spectrom.*, 2000, **197**, 1.
- 15 J. S. Becker, S. Boulyga, H.-J. Dietze, J. McLean and A. Montaser, 27th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, September 24–28, 2000, Nashville, Tennessee, USA, p. 104.