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BST thin films grown in a multiwafer MOCVD reactor

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Abstract

$(Ba_{0.7}Sr_{0.3})TiO_3$ thin films with a typical thickness of 30 nm were deposited on platinized wafers in a planetary multi-wafer reactor combined with a liquid delivery system. As a direct consequence of the reactor design, we obtain high film uniformity over 6 inch wafers as well as efficiencies for the precursor incorporation as high as 40%. The composition and microstructure of the films were routinely investigated by X-ray diffraction and X-ray fluorescence analysis. Further details of the microstructure were investigated by scanning electron microscopy. The electrical properties are characterized in terms of permittivity, loss angle, leakage current and the response to DRAM pulses and characteristic values obtained for depositions at 625°C include a specific capacitance of 60 fF/μm^2, a tanδ of 0.002 and leakage currents in the order of 10^{-10} A/cm^2 at 1 V. The electrical properties are discussed in relation to the microstructure and stoichiometry within a wide range of parameters.

Keywords: $BaTiO_3$ and titanates; Dielectric properties, electrical properties; Thin films; X-ray methods

1. Introduction

$(Ba_xSr_{1-x})TiO_3$, (BST), is one of the prime candidates as a high-k-dielectric in integrated high-density capacitors for future multi-GBit DRAM memory cells[1] and remarkable progress has been achieved in the metal-organic chemical vapor deposition (MOCVD) of thin BST films.[2–5] Most of the experimental reactors used for the development of mass production tools presently have a conventional single wafer showerhead design,[3–5] and we report as a comparison on the performance of a planetary multi-wafer reactor offering extremely high throughput due to possible batch mode processing which results in low cost of ownership.

In the second part, we report on the properties of BST films which were deposited on $Pt/TiO_2/SiO_2/Si$ wafers. The composition and microstructure of the films were routinely investigated by X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis using different calibration standards prepared by chemical solution deposition. Substrates without Ti adhesion layer were used additionally for the XRF analysis since the penetration depth of the X-ray beam is too large to distinguish the Ti of the BST from the Ti of the adhesion layer. Further details of the microstructure were investigated by scanning electron microscopy (SEM). The electrical properties were investigated after sputter-deposition and structuring of a Pt top electrode.

2. Thin film deposition

An AIXTRON 2600G3 Planetary Reactor® was used which can handle five 6-inch wafers simultaneously. The gas inlet is in the center of the reactor providing a pure horizontal gas flow, which makes this reactor a radial flow system. A liquid precursor delivery system, ATMI-300B,[6] mixes the liquid precursors of three different sources: 0.35 molar solutions of $Ba(thd)_2$ and $Sr(thd)_2$ and a 0.4 molar solution of $Ti(O\text{-}iPr)_2(thd)_2$. The liquid mixture is delivered by a micro-pump to the vaporizer on top of the reactor. Hot argon gas at the evaporation temperature of 235°C carries the evaporated solution through a quartz nozzle to the substrate. All MOCVD

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experiments were carried out at reduced pressure (below 2 mbar) in order to increase the gas diffusivity and prevent pre-reactions. The deposition temperatures varied between 565 and 655°C. The process conditions are summarized in Table 1.

The efficiency of the precursor use, defined as the ratio of the quantity deposited on all 5 wafers and the amount of the individual precursor elements contained in the consumed liquid, is an important parameter for the costs of ownership. The observed values of 45% for Ti and of 35–40% for Ba and Sr are extraordinarily high as compared to values reported for conventional showerhead reactors.[3] As these efficiencies were similar for the range of temperatures investigated, we may conclude that all depositions were achieved within the mass-transport limited reaction range. This behavior is partly due to the rather slow growth rate (≈3 nm/min) used here (however, the total throughput corresponds to a five time larger growth rate in a single wafer reactor). Finally, due to the gas-foil rotation principle we obtained a good homogeneity of the stoichiometry and film thickness over 6 inch wafers (< 1% standard deviation).[7]

3. Film structure and electrical properties

BST properties depend critically on the stoichiometry, the microstructure, as well as on the thickness of the films. For the present discussion, we select films of a composition around $(Ba_{0.7}Sr_{0.3})TiO_3$, and a thickness of 30 nm, which is close to envisaged application for DRAMS. Through process variations, we grew a broad field of BST thin films with different stoichiometry. As can be seen in Table 2 we selected films which are slightly Ti rich to discuss the influence of the growth temperature (565–655°C) on microstructure and the electrical properties; the influence of the sample stoichiometry is discussed additionally for films deposited at 625 and 565°C.

3.1. Film structure

Fig 1a shows the XRD patterns of slightly Ti-rich films deposited at different temperatures on Pt-substrates with a strong (111)-texture. We observe a very strong (100)-texture for depositions above 595°C and a transition to more polycrystalline and finally poorly crystalline growth at lower temperatures. The (100)-oriented films observed at high deposition temperatures show a width of the rocking curves of only 2–3° as this width is similar to that of the underlying Pt,[7] we observe a nearly epitaxial growth.

This perfectly columnar growth is further documented by the details of the line profiles as shown in Fig. 1b: thickness fringes are clearly visible in high resolution scans. The wavelength of the oscillations, $\Delta\theta$, yields immediately the film thickness, d:

$$d = \lambda/(2\Delta\theta\cos\theta) \quad (1)$$

Table 1
Typical deposition conditions

Substrate temperature	565–655°C
Reactor pressure	2 mbar
O_2 flow rate	50–500 sccm[a]
N_2O flow rate	50–500 sccm
Liquid source feeding rate	0.08 ml/s
Vaporization temperature	225–245°C
Film thickness	30 nm

[a] sccm: Standard cm^3 per min.

Table 2
Selected samples in the temperature-stoichiometry space; the selected samples are characterized by the values of the relative permittivity, ε_r

ε	Stoichiometry (GrII/Ti)						
Temperature	< 0.90	0.91–0.94	0.95–0.98	0.99–1.01	1.02–1.05	1.06–1.09	> 1.10
655°C			(151)				
625°C	161	179	208		185		
595°C			156				
580°C			158				
565°C	106	115	103	107	91	115	100

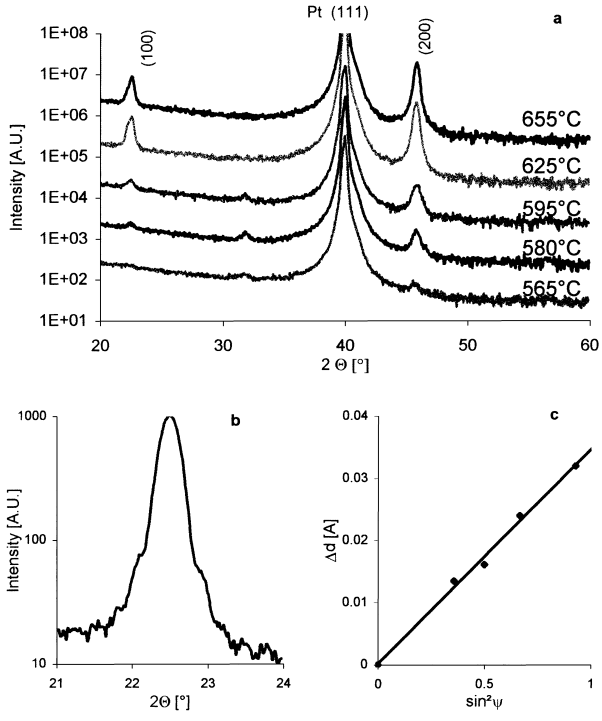

Fig. 1. (a) XRD-diagrams for films deposited at different temperatures: 655, 625, 595, 580 and 565°C. All films are slightly Ti rich, (GrII/Ti = 0.95–0.97). (b) High resolution scan of the (100)-reflection showing thickness oscillations for the example of sample grown at 625°C. (c) Evaluation of the film strain in a $\sin^2\psi$ plot for sample grown at 625°C.

λ is the wavelength of the CuK_α radiation used. The thickness obtained for the example shown in Fig. 1b is 30.1 nm which is in very good agreement with the XRF estimation of 30.7 nm obtained using the ideal density of BST of 5.758 g/cm^3. Combination of these results indicates perfectly mono-crystalline films and sharp interfaces. The absolute position of the lattice parameter is, however, smaller than the expected bulk value. This difference is due to the tensile stress of the film, which is thermally induced during cooling down of the film. This stress arises from the different thermal expansion coefficient of BST (and similarly for Pt) and of the Si-substrate. Detailed strain measurements are shown in Fig. 1c which yield the expected straight line in a $\sin^2\psi$ plot. The extrapolated value of Δd at $\sin^2\psi = 1$ corresponds to the tetragonal distortion of the film which can be quantified by the distortion $\varepsilon = \Delta d/d$ or by the c/a-ratio $= (d + \Delta d)/d$. The observed strain corresponds to tensile stress within the film plane, $\varepsilon = -0.95\%$ or $c/a = 0.99$. For different films this strain varied between 0.6 and 1.1%, due to variations in the quality of the film and the Pt electrode. However, no systematic dependence on the deposition temperature was observed. From this distortion the film stress, σ, can be estimated using reasonable values for the elastic constants of BST ($E = 107$ GPa, and Poisson number, $\nu = 0.3$):

$$\sigma = E/(\nu + 1)\varepsilon \quad (2)$$

Stresses between 500 and 900 MPa were observed. The c/a-ratio is always smaller than 1, i.e. opposite to the ferroelectric phase which is characterized by a larger c-axis. The substrate induced opposite distortion yields therefore a plausible argument for the suppression of the phase transition in these films.

This perfect (100)-growth is stable over a rather wide range of stoichiometries (GrII/Ti = 0.92–1.03), and only if the films are far off (0.74 in the example), there is polycrystalline growth. Similarly, the polycrystalline structure observed at 565°C does not change much with stoichiometry, however, there is indication for a steady increase of the (h00)-type reflections with increasing Group-II content of the films.

SEM micrographs, Fig. 2A and B, shows columnar growth and an in plane grain size in the order of the film thickness (30 nm) after high temperatures depositions. The films appear to be very smooth with a rms-surface roughness of 2–4 nm as shown by atomic force microscopy. For the films deposited at the lowest temperature (565°C) the column growth seem to be partly interrupted, the films appear hazy and the surface roughness is increased.

3.2. Electrical properties

For the electrical characterisation Pt top electrodes were deposited by magnetron sputtering. Electrode sizes of a diameter between 0.1 and 1.13 mm were obtained by a lift-off process. An additional post-annealing was performed ex situ. The standard characterisation included the dielectric permittivity, ε_r, and the dielectric loss, tanδ. More detailed investigations include the leakage current, the frequency dependence of the relative permittivity and the relaxation characteristics as well as the response to DRAM pulses. All measurements were performed at room temperature.

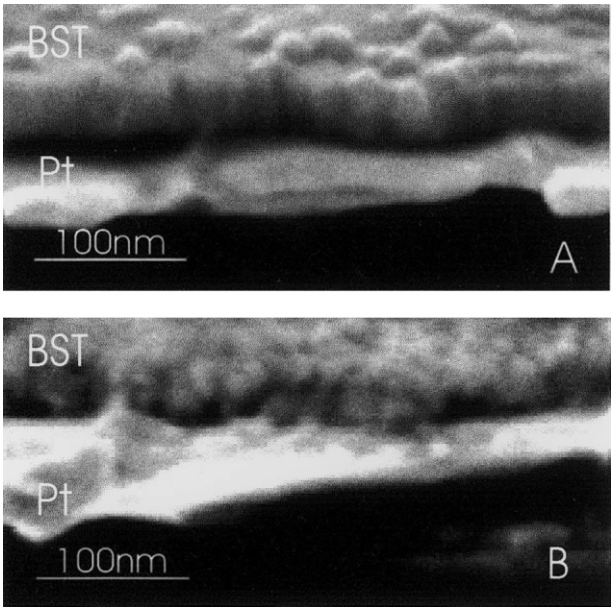

Fig. 2. SEM micrographs for Ti-rich samples (GrII/Ti = 0.95–0.97) deposited at (A) 625°C showing perfect columnar growth and (B) 565°C showing occasionally interrupted columns.

Table 2 summarises the permittivity data measured at a frequency of 1 kHz and an oscillator voltage of 50 mV. We observe a strong influence of the deposition temperature (or microstructure as discussed above): the ε_r value decreases for decreasing deposition temperatures. The value at 655°C is in parentheses as the deposition conditions for the XRF reference sample were not exactly the same. In particular, we obtain a typical value of $\varepsilon_r \approx 208$ for Ti-rich films (GrII/Ti≈0.97) grown at 625°C, which corresponds to a specific capacitance of $C/A = 59.1$ fF/μm^2. For a film at 565°C this value is reduced to $\varepsilon_r \approx 110$ or 30.2 fF/μm. Permittivity depends also on the stoichiometry and reaches its maximum just below the exact stoichiometric composition for samples grown at 625 °C. However, at the low temperature regime (565°C) the permittivity is not seriously affected by the film composition.

Similar to earlier results[7] we observe an almost constant dispersion of the permittivity over the whole frequency range from 1 Hz to 1 MHz: e.g. a change of 0.45%/decade for a Ti-rich film (GrII/Ti≈0.97) grown at 580°C. The dissipation factor has values between 0.002 and 0.004 and shows no systematic variation

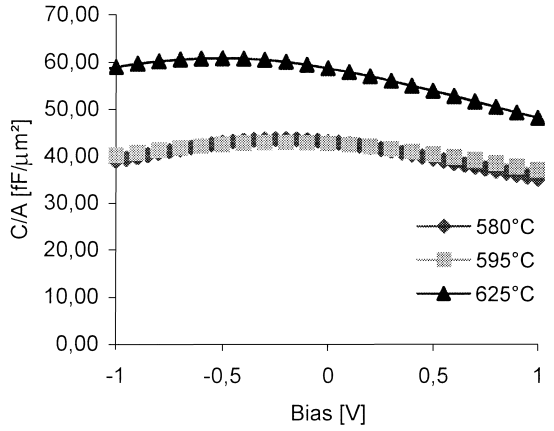

Fig. 3. C(V) curves for Ti-rich samples (GrII/Ti = 0.95–0.97) grown at 625, 595 and 580°C.

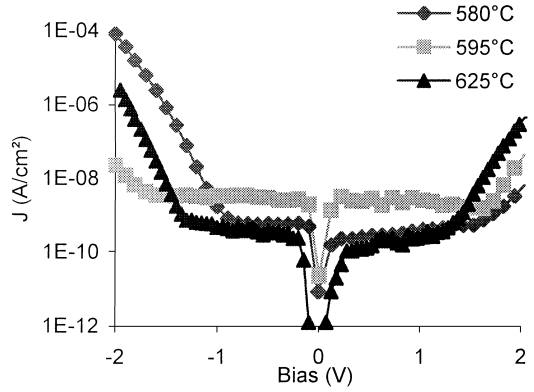

Fig. 4. Leakage currents for the same samples as in Fig. 3.

within the investigated range of stoichiometry and deposition temperature.

Fig. 3 shows the bias voltage dependence of the specific capacitance for Ti rich samples (GrII/Ti≈0.97) deposited between 580 and 625°C. The obtained curves are asymmetrical with an additional offset of the curve maximum of app. 0.2 V to negative values. This effect seems related to our present electrode deposition and treatment and is under investigation. Similar to the C(V) curves, the leakage currents, Fig. 4, also display this asymmetry. Deposition temperatures above 580°C yield values for the leakage current in the order of 10^{-10} A/cm^2 at 1 V bias.

The DRAM pulse measurements were performed for all films in the focused region. The capacitors were fully charged with sufficiently long pulses. Fig. 5 shows the DRAM characteristics for a sample grown at 625°C. After application of a 400 kV/cm (1.3 V) field we obtain 4% voltage drop in the first second after pulse load. All samples displayed only slight loss of charge no more than 5% up to a field of 300 kV/cm, which corresponds to a bias voltage of 1 V. Extraordinary good DRAM behavior was presented for the 595°C sample, e.g. 1 s after a 700 kV/cm (2.3 V) pulse the voltage drop was

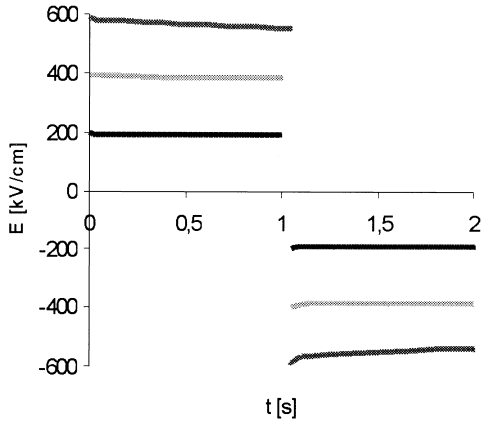

Fig. 5. DRAM pulse tests with different pulse amplitudes for a slightly Ti-rich sample deposited at 625°C.

4.2%. Additionally, we always observe symmetrical behavior after polarisation reversal up to a 300 kV/cm field. Above this field this symmetry is distorted and an exponential voltage drop can be detected.

4. Summary and conclusion

$(Ba_{0.7}Sr_{0.3})TiO_3$ films of 30 nm thickness were grown at different deposition temperatures and with different stoichiometry within a planetary reactor and structure property relations could be investigated within a broad range of parameters.

For deposition temperatures around 600°C we obtain a perfect (100)-fiber structure on Pt-(111) which is revealed by thickness fringes in the XRD scans. SEM shows columnar growth with in plane grain sizes of 30 nm. Electrical data are suitable for DRAM application, e.g. $c/a \approx 60$ fF/µm^2 and $J = 3{,}7 \cdot 10^{-10}$ A/cm^2 at 1 V. At the lowest deposition temperature of 565°C polycrystalline growth is observed and the columnar growth seems interrupted. Nevertheless, electrical data, $c/a \approx 30$ fF/µm^2, are still in a range suitable for DRAM application.

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