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Chemical Route to Ferroelectric Thin Film Capacitors

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Abstract

For the first time the fabrication of ferroelectric $SrBi_2(Ta,Nb)_2O_9$ thin film capacitors with RuO_2 electrodes is conducted using a full chemical route. $SrBi_2(Ta,Nb)_2O_9$ sols were obtained from niobium and tantalum ethoxides mixed with bismuth and strontium 2-ethylhexanoates. RuO_2 sols were prepared by dissolving an aqueous solution of ruthenium nitrosylnitrate into 2-methoxyethanol. Capacitors were fabricated by spin coating the precursor solutions on silicon wafers according to the Si/RuO_2/$SrBi_2(Ta,Nb)_2O_9$/RuO_2 sequence. Fully crystallized crack-free materials (RuO_2 and $SrBi_2(Ta,Nb)_2O_9$) were obtained by annealing at 700°C for 2 h. Hysteresis loops (3–10 V) are similar to those observed using platinum electrodes. *© 1999 Elsevier Science Limited. All rights reserved*

Keywords: films, sol–gel processes, Aurivillius phases, ferroelectric properties.

1 Introduction

Layered bismuth oxide ferroelectric thin films have attracted considerable attention for applications to non-volatile ferroelectric random-access memories and a number of international patents devoted to their preparation and properties have been taken out.[1–3] $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ are part of the so-called Aurivillius phases with general formulas $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$ with $m=2$.[4] Recently such thin films have been found to show very high fatigue behaviour resistance, especially when elaborated with ruthenium oxide electrodes.[3,5,6] Top and bottom electrodes—e.g. platinum, $(La,Sr)CoO_3$ or RuO_2—were generally deposited by physical vapor deposition.[7–10]

As there were no mention in literature concerning the fabrication of both top and bottom electrodes by sol–gel spin coating onto chemically prepared Aurivillius thin films, a study was started on the possibility of fabricating thin films capacitors by successive spin-coating of RuO_2, $SrBi_2(Nb,Ta)_2O_9$, and RuO_2.

The present paper deals with the chemical preparation of RuO_2, $SrBi_2(Nb,Ta)_2O_9$, and RuO_2/$SrBi_2(Nb,Ta)_2O_9$/RuO_2 thin films and their characterisation using temperature-programmed X-ray diffraction, scanning electron microscopy and electrical measurements.

2 Experimental

2.1 Preparation of the precursor solutions

Appropriate $SrBi_2Nb_2O_9$ (SBN), $SrBi_2Ta_2O_9$ (SBT), $SrBi_2(Nb,Ta)_2O_9$ (SBNT), precursor solution (0·3 mol l^{-1}) was prepared first by dissolving strontium 2-ethylhexanoate in 2-ethylhexanoic acid at 120°C, then addition of bismuth 2-ethylhexanoate, and finally addition of niobium and/or tantalum ethoxide previously dissolved in ethanol.

Ruthenium dioxide precursor solutions were prepared by dissolving 0·01 mol of a ruthenium(III)-nitrosylnitrate $Ru(NO)(NO_3)_3$ aqueous solution in enough 2-methoxyethanol to achieve a final concentration of 0·29 mol l^{-1}. This molarity would insure good spin coating conditions, eg. film thickness and adhesion on the substrate as well as on the ferroelectric film.

2.2 Spin-coating

Films were obtained by spin-coating precursor solutions at 4000 rpm for 30 s on to Si wafers using a Sulzer photoresist spinner. The coating was then dried at 300°C for 10 min to remove organics. Each

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coating gave a film about 30 nm thick. Deposition, drying and pyrolysis steps were repeated up to 15 times to prepare films with various thickness. Pure and well-crystallised SBN, SBT and SBNT thin films were obtained after annealing at 700°C for 2 h. Similar conditions were used for the deposition of RuO_2 bottom and top electrodes. Top electrodes areas were about 0·1 mm^2.

2.3 Characterisation of the deposited films

The crystallisation of the films was followed by temperature-programmed X-ray diffraction in air at various temperatures ranging from 20 to 800°C, using a Siemens D5000 diffractometer (θ/θ, Cu K_α radiation) fitted with a high temperature furnace (Anton Paar HTK10, Pt heating sample holder). Morphology and surface microstructure of the thin films were observed by scanning electron microscopy (Philips XL30). The resistivity measurements of RuO_2 films were carried out using the conventional four-point probe method, with four sputtered gold electrodes. The resistivity was measured at room temperature as a function of film thickness and annealing temperature. Hysteresis cycles were obtained using the Radiant Technologies RT 66A pulsed testing system.

3 Results and Discussion

3.1 Structural and electrical characterisation of RuO_2 films

Preliminary experiments have shown that the crystallisation starts at about 260°C and is complete at 700°C. So, all the thin films investigated in this study were heated at this temperature for 2 h to insure full crystallisation before microscopic observations. The lattice parameters calculated from X-ray diffraction patterns of annealed films (Fig. 1) are not significantly different from those obtained from powders [a = 0·4486 (0·0009) nm; b 0·3102 (0·0009) nm].[11]

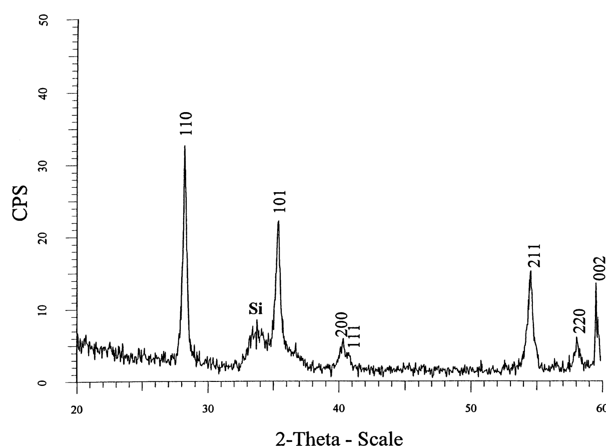
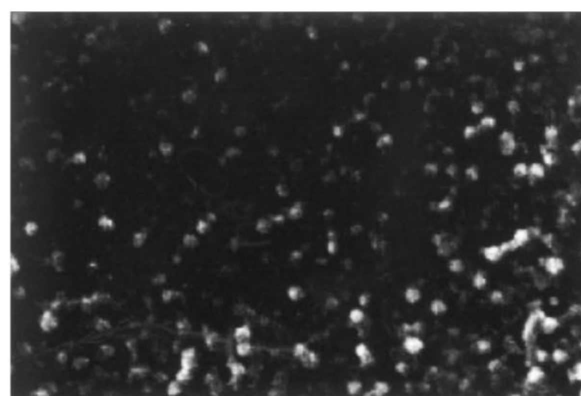


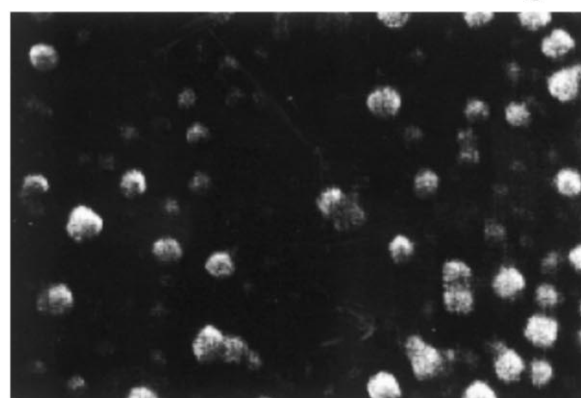
Fig. 1. Room temperature X-ray diffraction patterns of a 300 mn-thick RuO_2 film.

As a consequence, the films prepared using the above mentioned conditions are actually made of the pure stoichiometric RuO_2 phase.

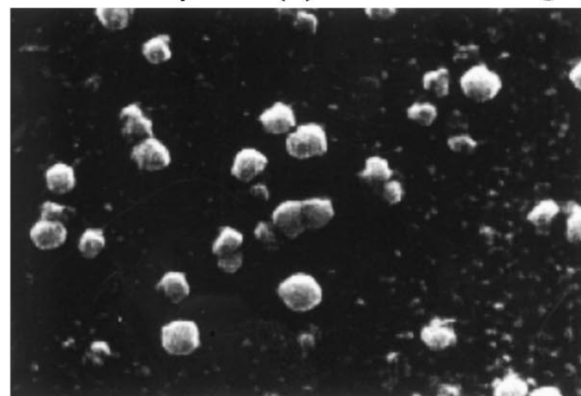
Whatever the thickness, very dense and homogeneous microstructure was observed. As the number of successive coatings increases from 5 to 10, the grain size increases from 100–150 to 200–250 nm [Fig. 2(a) and (b)]. For 15 coatings, the average grain size does no longer increase but some grains became larger either by coalescence of smaller grains or by crystal growth in a direction perpendicular to the film surface [Fig. 2(c)].



1 μm (a) 5 coatings



1 μm (b) 10 coatings



1 μm (c) 15 coatings

Fig. 2. SEM micrographs of multi-coatings RuO_2 films after annealing at 700°C for 2 h.

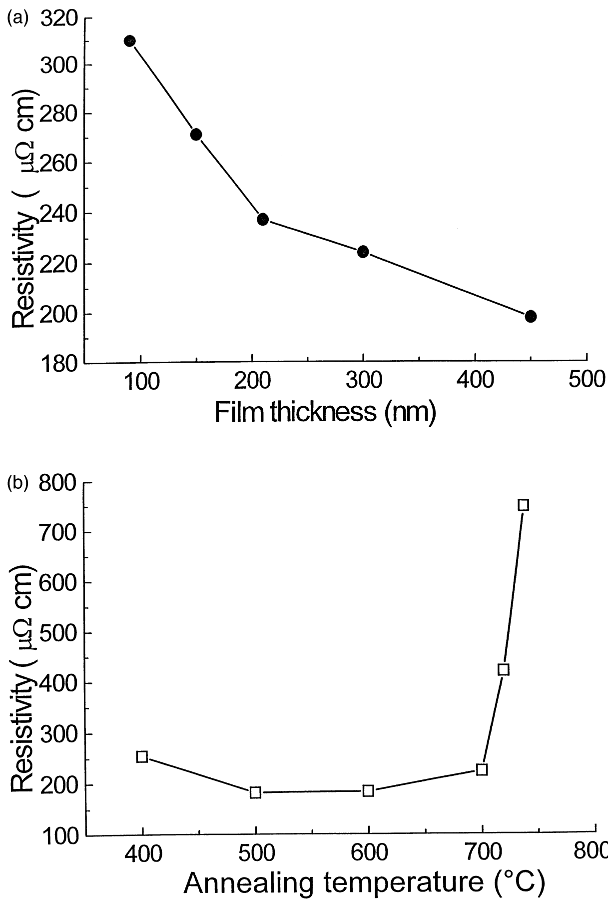


Fig. 3. Resistivity of RuO_2 films as a function of (a) thickness and (b) annealing temperature.

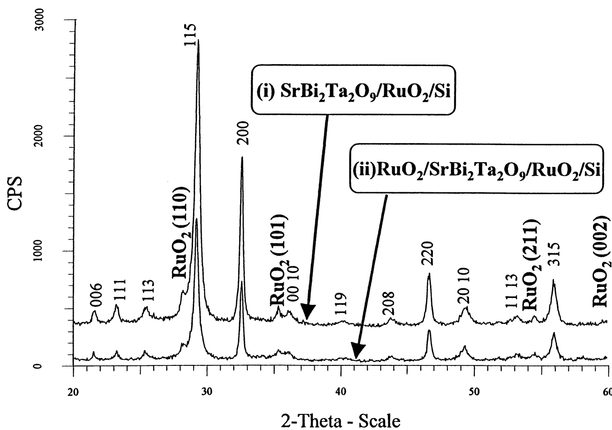


Fig. 4. X-ray diffraction patterns of $SrBi_2Ta_2O_9$ film on RuO_2-spin-coated Si substrates (i) as prepared ($SBT/RuO_2/Si$), (ii) spin-coated with RuO_2 ($RuO_2/SBT/RuO_2/Si$).

The electrical resistivity of the films was measured as a function of the final thickness, i.e. as a function of the number of coatings. It strongly decreases as the thickness increases and reaches a value less than 200 $\mu\Omega$ cm, about 6 times the value of bulk material for a 450 nm-thick film [Fig. 3(a)]. Annealing the films at increasing temperatures up to 700°C did not make the resistivity change significantly but at higher annealing temperatures the resistivity increased steeply, mainly because of the decomposition of RuO_2 and silicon diffusion into the film [Fig. 3(b)].

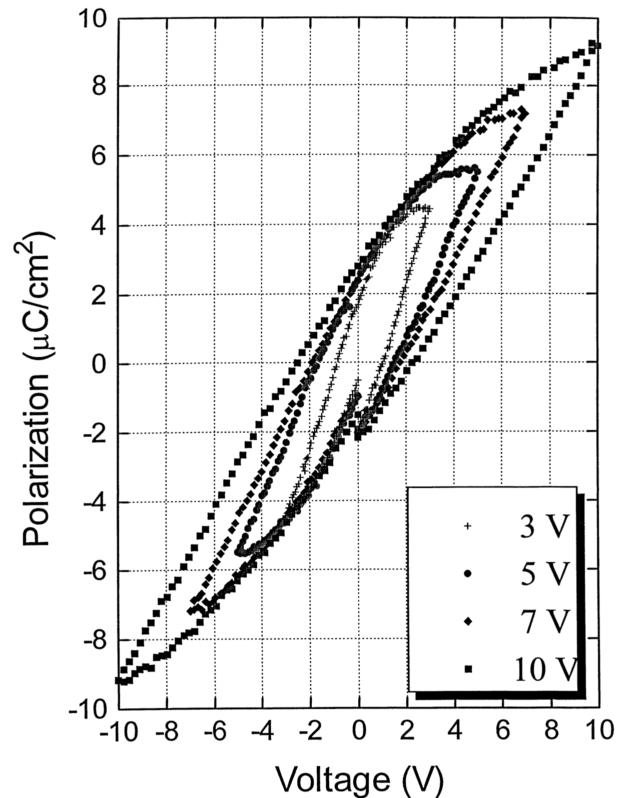


Fig. 5. Hysteresis curves of $RuO_2/SBT/RuO_2/Si$ capacitors for several applied voltages.

3.2 Structural and electrical characterisation of SBN, SBT and SBNT thin film capacitors

SBN, SBT and SBNT films were deposited onto RuO_2 spin-coated Si wafers following the same deposition process. In Fig. 4, which shows the X-ray diffraction patterns of 10 successive SBT coatings, the main RuO_2 reflections are still visible as the ferroelectric film does not fully absorb the incident X-ray beam. No significant change was observed when RuO_2 film was subsequently spin coated. As far as is known, it is the first time that a full chemically processed thin film capacitor with no metal electrodes is prepared.

Hysteresis loops were obtained under applied voltage ranging from 3 to 10 V (Fig. 5). The characteristics are similar to those measured using platinum bottom and top electrodes. However, the loops do not show full saturation of the polarisation and therefore these capacitors would not be able to retain polarised state for a long time. To be usable as non-volatile memories such multilayers need to be improved, especially concerning both the conductivity of RuO_2 electrodes and the quality of the RuO_2–SBNT interfaces.

4 Conclusion

$SrBi_2(Nb,Ta)_2O_9$ ferroelectric thin film capacitors with RuO_2 electrodes were prepared for the first time by a full chemical route using the spin-coating technique. They show room temperature ferroelectric behavior comparable to similar materials prepared by other physical or chemical deposition processes. Further fatigue experiments and structural investigations at the RuO_2/SBNT interface are now in progress.

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