Low temperature crystallization of SrBi₂Ta₂O₉ thin films using microwave oven

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Received 23 January 2003; received in revised form 14 January 2004; accepted 3 February 2004
Available online 12 April 2004

Abstract

SrBi₂Ta₂O₉ thin films, produced by the polymeric precursor method, were crystallized at low temperature using a domestic microwave oven. A SiC susceptor were used to absorb the microwave energy and rapidly transfer the heat to the film. Low microwave power and short time have been used. The films thus obtained are crack-free, well-adhered, and fully crystallized, even when treated at 600 °C for 10 min. The microstructure displayed a polycrystalline nature with an elongate grain size comparable to the films obtained by the conventional treatment. The dielectric constant values are 240, 159 and 67, for the films treated at 600 °C, 650 °C and 700 °C, respectively, when the films are placed directly on the SiC susceptor. Electrical measurements revealed that the increase of the temperature treatment to 700 °C causes a complete loss of ferroelectricity due to degradation of the bottom interface. A 4 mm-ceramic wool put between the susceptor and the substrate minimizes the interface degradation leading to a dielectric constant, a dielectric loss, and a remnant polarization (2P_r) of 181 μC/cm², 0.032 μC/cm², and 12.8 μC/cm², respectively, for a film treated at 750 °C for 20 min.

Keywords: SrBi₂Ta₂O₉; SBT; Thin film; Ferroelectric; Microwave; Crystallization

1. Introduction

Ferroelectric materials have been extensively studied in thin film form, mainly for application as non-volatile ferroelectric memories (FeRAM). The most extensively studied material for this application is PZT, which presents a serious fatigue problem after several polarization–depolariization cycles when deposited on Pt [1]. These problems can be overcome if oxide electrodes are used, but this solution is not cost effective for IC technology. That is why the search for alternative materials is incessant and the compounds belonging to the Aurivillius family, Bi₂O₂⁺ (A m – iBnO₃m+1)₂⁺, (BIT – Bi₄Ti₃O₁₂, SBN – SrBi₂Nb₂O₉, SBT – SrBi₂Ta₂O₉), are considered to be almost fatigue-free and potential candidates for FeRAM applications [2,3].

Among these compounds, SBT has received a great deal of attention due to its high transition temperature (T_c approx. 330 °C). However, to obtain well crystallized SBT films with ferroelectric properties, a relatively high temperature (approx. 800 °C) is required; moreover, the films must be kept at this high temperature for at least 1 h [4,5]. This long thermal treatment seriously damage the stack, leading to interdiffusion between elements of the film and substrate and, in some cases, can cause loss of the films’ stoichiometry (if volatile elements are present). Therefore, for SBT films to be used in FeRAM applications, it is imperative to decrease the temperature and/or the thermal treatment time.

Rapid thermal treatment (RTA) has been used to reduce the time the stack is held at a such high temperature. Several authors [6–9] have used halogen lamps, which can provide a heating rate of 150 °C/s, with a thermal treatment ranging from 30 s to 5 min. The films, in some cases, displayed a well-crystallized perovskite phase. Some authors have
placed the film directly into the furnace at the temperature required for the thermal treatment and, after 5 to 10 min, have quenched the film to room temperature. However, in either case, post annealing for at least 1 h in a conventional furnace is usually necessary in order to produce well crystallized films [8,10].

A new tool for high-temperature processing of materials, microwave energy, has been developed in recent years. Much attention has focused on this technology due to the advantages it offers with microwave processing, including reduced processing costs, higher quality production, new materials and products, etc. [11–13].

This work investigated microwave energy as a rapid thermal route for the crystallization of SBT films, with the advantage of reducing the time and temperature of thermal treatments.

2. Experimental details

The SBT films were prepared with a chemical solution, whose detailed preparation method is published elsewhere [14]. Briefly, the chemistry used for SBT thin film preparation is based on strontium carbonate, bismuth oxide and tantalum ethoxide as the cation source. Strontium carbonate, SrCO$_3$, 99.9% (Merck), tantalum ethoxide, Ta(OCH$_2$)$_5$, 99.999% (Alfa Aesar), and bismuth oxide, Bi$_2$O$_3$, 99.999% (Aldrich) were used as reagents to synthesize SrBi$_2$Ta$_2$O$_9$. A tantalum citrate was formed by dissolving the tantalum ethoxide in a solution of citric acid dissolved in ethylene glycol. The Ta content was gravimetrically determined as Ta$_2$O$_5$. Stoichiometric amounts of SrCO$_3$ as salt, and Bi$_2$O$_3$ dissolved in water with HNO$_3$ were added to this tantalum citrate solution. Ethylenediamine was added drop by drop into the constantly stirred solution until the pH reached 7–8. After the solution became homogeneous, ethylene glycol was added as a second solvent. The molar ratio of strontium, bismuth and tantalum was 1:2:2, the citric acid/metal molar ratio was set at 3.95 and the citric acid/ethylene glycol ratio was set at 60/40 (mass ratio). A polymeric resin was obtained by reaction of the metallic citrates with ethylene glycol and ethylenediamine. The viscosity of the solution was adjusted by water evaporation until it reached 25 MPa s.

The films were deposited onto Pt/Ti/SiO$_2$/Si substrates by spinning the deposition solution at 7000 rev./min for 20 s. After deposition, the films were treated at 400 °C for 2 h to eliminate any remaining organic material. The desired thickness was obtained by several cycles of deposition and thermal treatment at 400 °C. The films were crystallized at 600, 650 and 700 °C for 10 min in a domestic microwave oven using a SiC susceptor, which absorbs the microwave energy and rapidly transfers the heat to the film. No post annealing treatment was performed after crystallization.

Fig. 1 gives a schematic illustration of the film’s crystallization inside the microwave oven. The film was placed over the SiC susceptor, which was coupled to a thermal insulator. The temperature was measured with a K-type thermocouple placed 4 mm above the film, and the oven’s maximum heating rate was used, i.e. approximately 237 °C/min. The film was cooled at the rate allowed by the susceptor and the insulating material. A thermocouple thermometer (FLUKE, 54 II) was used to determine the heating profile in each case.

After crystallization, the films were characterized by X-ray diffraction (Rigaku, DM Max 2500 PC), 40 kV and 150 mA from 20 to 60° 2θ, to monitor the phase evolution. Atomic force microscopy (AFM) (Digital, NanoScope 3A) was used to examine the films’ surface morphology and microstructure. Scanning electron microscopy (SEM) (Zeiss, DSM 940A) was used to measure the thickness, while the cross section microstructure was evaluated by field emission scanning electron microscopy (FE-SEM) (PHILIPS, XL30).

For the electrical measurements, Au upper electrodes, each with a nominal area of 7.07 × 10$^{-4}$ cm$^2$, were sputter-deposited through a shadow mask. Before taking the electrical measurements, the Au/SBT/Pt capacitors were annealed at 200 °C for 30 min to improve the electrode/film contact. The dielectric measurements were taken with a HP 4194A impedance analyzer and the hysteresis loops were measured with a ferroelectric tester (Radiant, RT6000HVS). A source measure unit (KEITHLEY 237) was used to take current vs. voltage measurements.

3. Results and discussion

Fig. 2 shows the XRD patterns for the films treated at 600, 650 and 700 °C in the microwave oven. As can be seen, even at 600 °C the film displayed a well-crystallized perovskite phase. No significant changes were observed as the temperature rose to 700 °C. The films were polycrys-
talline without preferential orientation, and no secondary phases were detected. For comparison, the XRD pattern of a film crystallized at 700 °C for 2 h in a conventional furnace is also shown (Fig. 2d). The only detectable difference in the XRD patterns is a small shift to small angles of the 115 peak, possibly indicating a different thermal stress in the film crystallized in the conventional furnace.

Fig. 3 shows the microstructure, observed by AFM, of the films treated for 10 min in the microwave oven at 600, 650 and 700 °C, revealing a well defined grain structure even when treated at 600 °C. The elongated grains are characteristic of bismuth-layered compounds with good crystallization and the microstructure is comparable to that of films obtained by the conventional treatment [14]. As the temperature increased to 700 °C, the grains became larger and the film less dense than films treated at lower temperatures. In addition, the surface roughness increased from 7.8 nm to 11.0 nm as the temperature rose from 600 to 700 °C.

Fig. 4 shows the measurements of the dielectric constant as a function of the frequency. The dielectric constant and the dissipation factor, measured at 100 kHz frequency in the films treated at 600 °C, 650 °C and 700 °C were, respectively, 240, 159 and 67, and 0.085, 0.18 and 0.044. Considerable dispersion can be observed in the frequency range (from 100 Hz to 10 MHz) of 30–45% in the films treated at 600 and 650 °C, which may be attributed to space charges at the film/electrode interface. The film treated at 700 °C showed a lower dielectric constant, possibly due to the formation of an interfacial layer with a low dielectric constant, as observed previously by Hu et al. [6,7]. The high dielectric loss at low frequency in this film confirmed the presence of space charges at the electrode/film interfaces.

At the moment, it is impossible to state unequivocally that these space charges originated at the upper electrode/film interface as a result of the greater surface roughness. It was also found that the increase in surface roughness was accompanied by some hillocks, causing voids between the film and the lower electrode, which may have contributed toward the generation of some space charge and to the reduction of the dielectric constant as the temperature rose. So far, the origin of the voids observed here is still unknown.

The $C-V$ measurements of the films treated at 600 and 650 °C displayed a butterfly-like curve (Fig. 5) characteristic of a ferroelectric material, but the non-linear variation of the capacitance according to the applied voltage disappeared in the film treated at 700 °C. The capacitance values decreased as the temperature of the thermal treatment increased. These findings strongly suggest that irreparable
degradation of the lower interface occurred when the film was treated at 700 °C for 10 min.

The ferroelectric measurements shown in Fig. 6 revealed the same behavior. The hysteresis loop of the film treated at 600 °C presented a remanent polarization ($2P_r$) of 10.6 μC/cm². The leakage current measurements showed a highly conductive film, even at 600 °C (approx. 1.3 mA/cm² at 2 V). As the temperature increased to 650 °C, the hysteresis loop broadened, also indicating high conductivity and, at 700 °C, the ferroelectric result was very poor.

Another possibility may have been damage suffered by the lower electrode/film interface. Since the susceptor was placed under the substrate, the film was crystallized by an upward heat flux coming from the film/substrate interface, so these voids may have originated from the stress caused by the dissimilar thermal expansion rates of the substrate and the film.

To verify the effect of the thermal treatment when the substrate was placed directly on the SiC susceptor, the cross section of the films was examined by FE-SEM, as shown by the results in Fig. 7. The Pt layer visibly suffered severe damage, and also presented some porosity. Delamination clearly occurred in the films treated at 600 and 700 °C (indicated by the arrows), confirming the interfacial damage. However, the heating rate used (237 °C/min) was much lower than that used in halogen RTA furnaces (approx. 150 °C/s). The microwave energy probably plays an important role in addition to simply heating the susceptor, but that role is not yet clear.

At this point the question was: what could be causing such an effect on the lower interface? Perhaps the nominal temperature was lower than the temperature of the SiC susceptor, so the film was possibly subjected to a much higher temperature than the measured temperature. Due to the electrical discharge between the SiC susceptor and the thermocouple (caused by the electric spark formed by the high electric field in the microwave environment), the temperature was measured by a thermocouple placed 4 mm above the film, as described earlier. To verify the susceptor’s heating profile, the susceptor and a second thermocouple were grounded, allowing the latter to be in contact with the susceptor so that the real temperature could be measured. The thermocouple normally placed at 4 mm from the susceptor measured the set temperature (for example, 750 °C) and the second thermocouple measured the temperature of the susceptor. Fig. 8a shows the temperature profile of the SiC susceptor. As can be observed, in 3 min, the temperature of the susceptor rose to approximately 880 °C, i.e. 130 °C higher than the nominal temperature. In other words, for
more than 4 min, the films may have been subjected to a temperature at least 100 °C higher than expected. The thermal shock, allied to the microwave effect, may have been the cause of the degradation of the lower interface.

To minimize the thermal shock caused by the rapid heating of the SiC susceptor, 4 mm-thick ceramic wool (Kaowoll 1600) was placed between the susceptor and the substrate. The low density of the ceramic wool prevents static charges from accumulating on the surface, thereby preventing electric sparks. Thus, the film was aligned with the thermocouple used for the temperature measurements. Fig. 8b depicts the temperature profile for a thermal treatment at 750 °C. It is important to emphasize that the maximum temperature recorded after 3 min was 793 °C, and the desired stabilization at 750 °C was reached after 4 min. These results suggest that the second experiment exerted a positive effect on the films’ properties.

An SBT film was then crystallized at 750 °C for 20 min by placing 4 mm thick ceramic wool between the susceptor and the substrate. The film thus obtained presented a dielectric constant and a dissipation factor of 181 and 0.032, respectively, measured at a 100 kHz frequency (Fig. 9). The higher dielectric constant value and the absence of dielectric loss at low frequency attest to the better quality of the capacitor.

Fig. 10a shows the cross section of the film with a 375 nm thickness, revealing a much denser lower electrode,
although the film is somewhat porous. The AFM measurements (Fig. 10b) revealed a porous structure of small rounded grains, very similar to those obtained by the conventional furnace method. Longer thermal treatment in the microwave oven and/or higher temperatures would probably yield higher quality films.

The electric measurements indicated that the film was still leaky \( (9 \times 10^{-5} \text{ A/cm}^2) \), but no breakdown was observed up to 10 V of applied voltage. The butterfly-like curve (Fig. 11a) confirmed the ferroelectricity of the film, but a very high applied voltage was required to completely invert the ferroelectric domains, as confirmed by the hysteresis loop (Fig. 11b), probably due to the film’s low density and small grain size. The remanent polarization was \( 2P_r = 12.8 \mu\text{C/cm}^2 \) at 18 V of applied voltage.

The fact that the XRD patterns showed no significant difference for the films placed directly on the SiC susceptor and treated at different temperatures suggests that thermal treatment in the microwave oven yields well crystallized SBT thin films without detectable secondary phases. These results represent a significant improvement, since the time spent on the treatment (10–20 min) is 6 to 12 times less than that reported for good crystallization of SBT films in conventional ovens, as shown in Table 1.

The high upward heat flux generated by the susceptor promoted interfacial nucleation of the crystalline phase in the film, which can be very useful when an epitaxial growth is desired. Epitaxial growth has been successfully achieved in LiNbO\(_3\) thin films deposited onto sapphire substrates and processed in a microwave oven [17]. Also, to minimize the effect of the drastic thermal shock when the film is placed directly on the susceptor, the alternative is to put the susceptor above the films. This arrangement, which favors the superficial crystallization of the film, is useful for obtaining polycrystalline films and has been tested with good results in SBN thin films [18].

These findings strongly encourage investigations into the crystallization of thin films using microwave energy. Studies are ongoing to optimize the maximum temperature and time required for good crystallization of SBT films using microwave ovens, without degradation of the electrical properties.

4. Conclusions

SBT thin films with good ferroelectric properties \( (2P_r = 12.8 \mu\text{C/cm}^2) \) were successfully crystallized using a low power microwave oven, with no post annealing treatment. The real temperature in the susceptor, for a nominal temperature of 700 °C in the thermocouple placed 4 mm above the film, may be approximately 100 °C higher, which, allied to the effect of the microwave energy, may cause degradation of the film/electrode interface and, hence, to a loss of ferroelectric properties. The structural and electrical properties improved when 4 mm thick ceramic wool was
placed between the SiC susceptor and the substrate. Optimization of the temperature and time, for good crystallization of the film without degradation of the interface, may lead to films of a quality comparable to that obtained in conventional ovens.

These results represent a significant improvement in time, which is at least 3 times less using the microwave oven, since the temperature is comparable to that reported for good crystallization of SBT films, i.e. approximately 700–800 °C.

Acknowledgements

The authors acknowledge the Brazilian financing agencies FAPESP, FAPEM and CNPq/FINEP.

References


Table 1

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<th>Ref.</th>
<th>Furnace</th>
<th>Temp. (°C)</th>
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<th>εr</th>
<th>tanδ (%)</th>
<th>2P0 (μC/cm²)</th>
<th>2Ec (kV/cm)</th>
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<td>n.r.</td>
<td>14</td>
<td>n.r.</td>
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<tr>
<td>[10]</td>
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<td>750/800</td>
<td>30 s/1 h</td>
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<td>n.r.</td>
<td>20</td>
<td>90</td>
</tr>
<tr>
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<td>2 min</td>
<td>320</td>
<td>2.7</td>
<td>28.6</td>
<td>102</td>
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<tr>
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<td>10 min</td>
<td>240</td>
<td>8.5</td>
<td>10.6</td>
<td>80</td>
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* Post annealing in a conventional oven for complete crystallization; n.r. – not reported.