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Structural Characterisation of Sol–Gel $SrBi_2Nb_2O_9$ Thin Film Deposited on (001) $SrTiO_3$ Single Crystal

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Abstract

$SrBi_2Nb_2O_9$ (SBN) thin films with thickness close to 30 nm were deposited on single crystalline (001) $SrTiO_3$ (ST) substrate by sol–gel spin-coating. After deposition, the films annealed for 30 min at several temperatures (500, 550, 600, 650 and 700 °C) were studied by X-ray diffraction using a home-made diffractometer operating in asymmetric reflection geometry. Crystallisation of the precursor as pure $SrBi_2Nb_2O_9$ occurs between 500 and 550°C. The normal orientation of the film occurs at 550°C, i.e. at the very beginning of the crystallisation process. Rocking curves of (0010) lines show their full widths at half maximum (FWHM) decrease from 2·5° (550°C) to 1·8° (700°C), indicating that the small remaining disorientation decreases with increasing annealing temperature. A full ϕ-scan study of selected reflections showed that the film is heteroepitaxied on the substrate such as $(001)_{SBN}//(001)_{ST}$ and $[100]_{SBN}//[110]_{ST}$. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: films, sol–gel processes, heteroepitaxy, X-ray methods, niobates.

1 Introduction

The strong recent interest in the ferroelectric thin films of layered bismuth oxides like $SrBi_2Ta_2O_9$ is mainly due to their ability to present very low fatigue when polarization switching occurs.[1] Up to now, a number of studies dealing with processing, ferroelectric properties as well as orientation of the thin films deposited onto several substrates have been performed in many laboratories or companies. Nevertheless only few papers reported on the very first stages of crystallisation process of sol–gel derived materials.[2] This paper details a specific study by X-ray diffractometry of the crystallisation process for the niobium analogue of $SrBi_2Ta_2O_9$, namely $SrBi_2Nb_2O_9$ hereafter designed as SBN, deposited by sol–gel spin coating on single crystalline (001) $SrTiO_3$ (ST) substrates and the epitaxial relationship between the ferroelectric film and the substrate.

2 Experimental

2.1 Preparation of the precursor solution and spin-coating

Appropriate $SrBi_2Nb_2O_9$ (SBN) precursor solution was prepared first by dissolving strontium 2-ethylhexanoate in 2-ethylhexanoic acid at 120 °C, subsequent addition of bismuth 2-ethylhexanoate, and finally addition of niobium ethoxide previously dissolved in ethanol.

SBN powders were obtained and characterised after heat treatment at several temperatures in an electric oven. Thin films were fabricated by spin-coating the precursor solution at 4000 rpm for 30 s using a Sulzer photoresist spinner onto single crystalline (001) $SrTiO_3$ substrate. Details concerning the characteristics of the whole process have been published elsewhere.[3]

2.2 Characterisation

The X-ray diffraction home-made set-up used in this study is schematically given in Fig. 1. The CuK_{α_1} X-ray primary linear beam was supplied by a rotating anode and highly collimated by a four-reflection monochromator.[4] The intrinsic divergence was 12″ and the wavelength dispersion was $1{\cdot}4\times10^{-4}$. The specimen holder was equipped with

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five motorised movements making it possible to record diffraction patterns of either polycrystalline samples or single crystals and highly oriented thin films. Diffracted beams were collected using a Curved Position Sensitive Detector (Inel CPS 120). This device combines the simplicity of the Debye–Scherrer geometry with the simultaneous collection of data over a large angular range, good counting statistics and rather short counting times.[5]

3 Results and Discussion

3.1 Crystallisation of powders and thin films

Figure 2 shows powder X-ray diffraction patterns of samples fired for 30 min at several temperatures between 500 and 700°C. The crystallisation begins between 500 and 550 °C. The pattern recorded after firing at 500 °C shows several very broad lines which can be assigned to the occurring of a fluorite-like structure.[2] This phenomenon, already observed for STN, is more pronounced at 550 °C. The fairly broad diffraction lines are obviously associated with a very small size of the crystallites. At 600 °C, the 'perovskite' Aurivillius phase begins to appear. Upon further heating at 650 °C, the perovskite phase peaks sharpen and increase to the detriment of those of the fluorite structure. At 700 °C, the sample is completely converted to the SBN Aurivillius phase. The line sharpening is likely connected with the expected increasing grain size. The fluorite-like phase could be therefore considered as a transient phase, which transforms into the perovskite (SBN) one at high temperature.

The thin films deposited on (001) $SrTiO_3$ single crystals following the process described before were analysed by grazing incidence X-ray diffraction. Figure 3 shows the patterns of a film annealed for 30 min at several temperatures (500, 550, 600, 650 and 700 °C) so that the effect of successive annealing is cumulative. As the incidence angle ($\omega = 0{\cdot}5°$) under which the sample was irradiated did not correspond to a specific crystal orientation, the diffraction pattern gave only evidence of randomly oriented grains. At 500–550 °C, these crystallites do not present the 'Aurivillius phase' type, but are completely converted into it at 600 °C. The weak

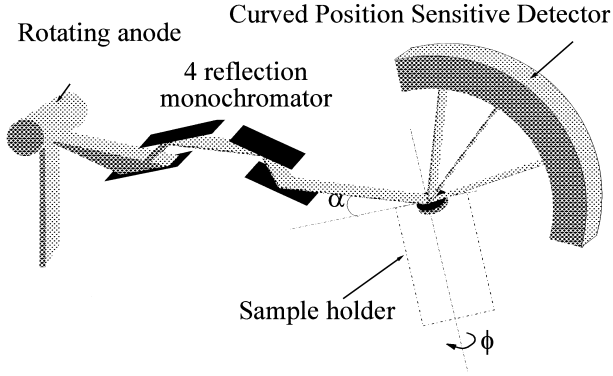

Fig. 1. X-ray diffraction set-up.

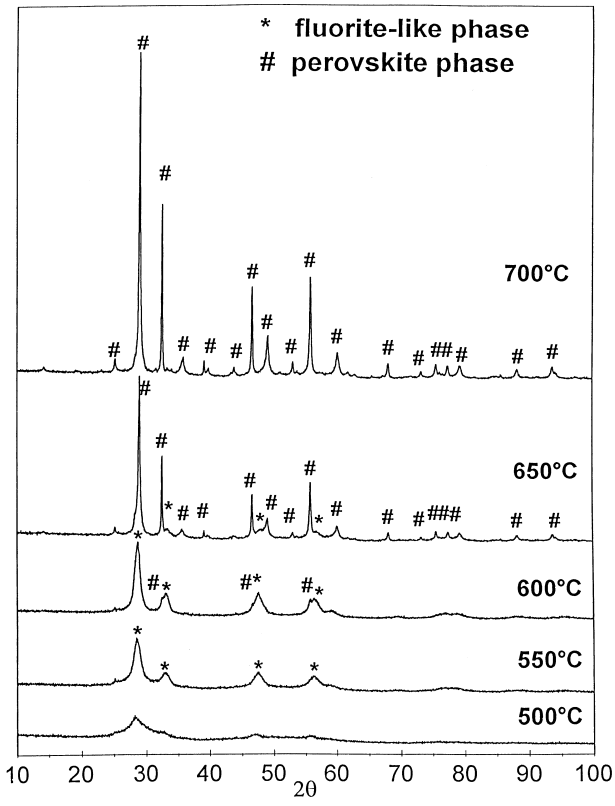

Fig. 2. SBN X-ray diffraction powder pattern at several annealing temperatures.

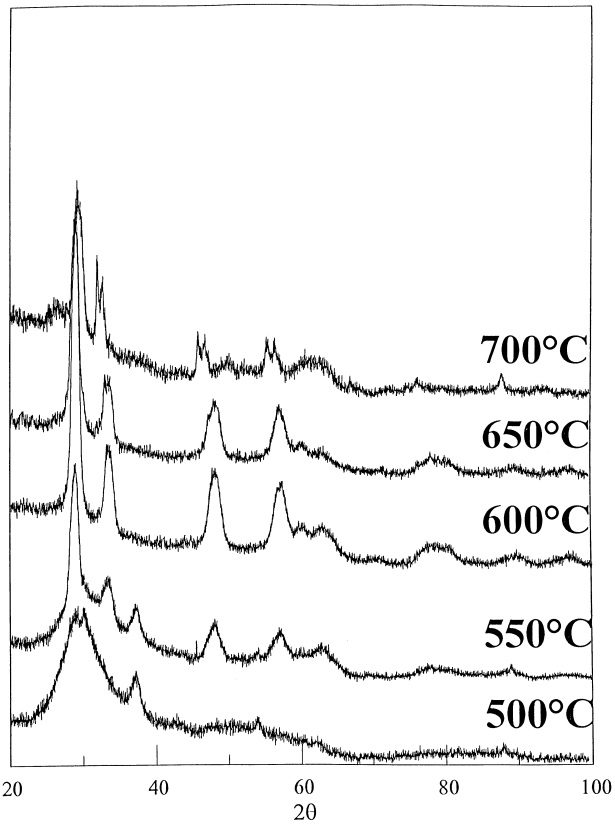

Fig. 3. Grazing incidence X-ray diffraction pattern of SBN thin film.

intensities of the diffraction lines and their decrease when the sample is annealed above 600 °C show that the number of disoriented grains is quite low and decreases with further annealing. These results support the assumption that a large part of the film would consist of highly oriented crystallites.

3.2 Heteroepitaxial growth

Previous studies have shown that such 'Aurivillius phases' thin films were often characterised by a (001)-type preferred orientation.[6] So further investigations were performed to improve the knowledge of such a phenomenon.

Using the experimental set-up described in Fig. 1, several X-ray diffraction patterns were recorded at incidence angles ω corresponding to the Bragg angles of some selected planes of the 'Aurivillius phase'. At every temperature, significant diffracted intensities were observed only when w was equal to the Bragg angles of the (001) planes. As an example, the patterns recorded for $\omega = \theta_{(0010)}$ are given in Fig. 4. They clearly show that the 'perovskite-type' grains are oriented as follows: $(0010)_{SBN}//(001)_{ST}$.

In Fig. 4, the inset shows the X-ray diffraction 'ω-rocking curves' of the (0010) reflection of the SBN film. Their full widths at half maximum (FWHM) decrease from 2·5° (550 °C) to 1·8° (700 °C), indicating that the small remaining disorientation decreases with increasing annealing temperature.

The in-plane orientation of the grains was studied by 180° ϕ-scans experiments with respect to the (113) $SrTiO_3$ planes. A typical ϕ-scan plot of the (2218) SBN line is given in Fig. 5. The intensity

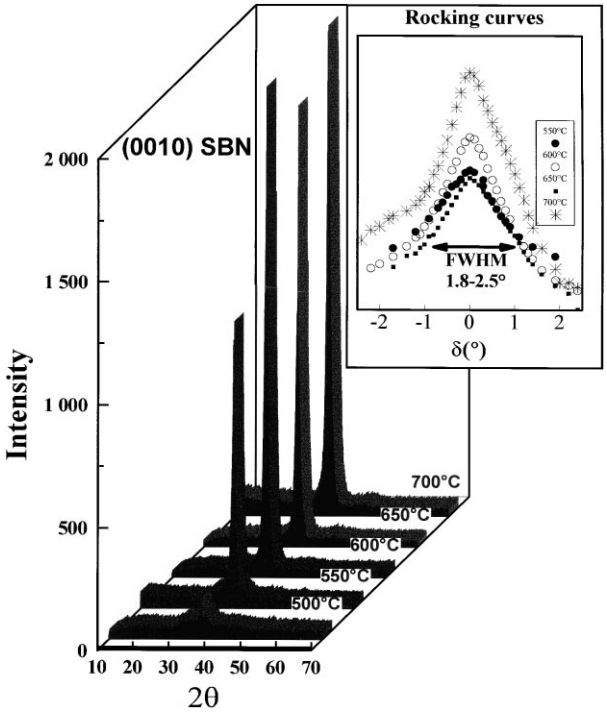

Fig. 4. (0010) lines X-ray diffraction pattern of SBN/ST thin flim at several temperatures.

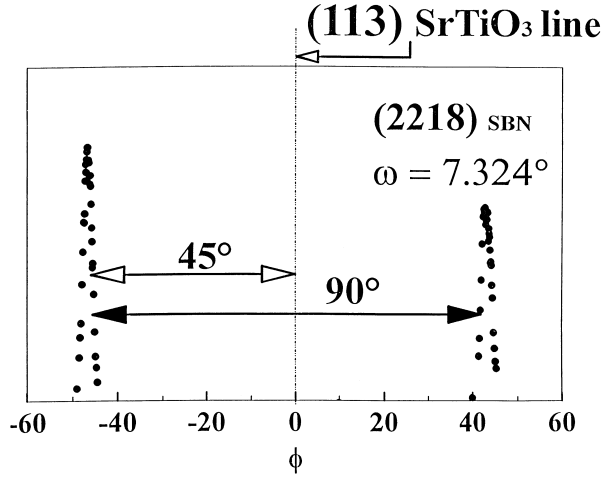

Fig. 5. ϕ-scans of $(2218)_{SBN}$ reflection with respect to $(113)_{ST}$ line (cf. Figure 1).

maxima occur at 90° from each other and at 45° from the (113) $SrTiO_3$ reference. The crystallites are therefore highly in-plane oriented in such a way that $[h00]_{SBN}$ would be parallel to $[hh0]_{ST}$. This result was expected as the a lattice parameters of SBN and ST are connected by the relationship $a_{SBN} = a_{ST}\sqrt{2}$.

4 Conclusion

By means of controlled incidence beam angle diffraction experiments, it was shown that sol–gel deposited $SrBi_2Nb_2O_9$ (SBN) thin films onto single crystalline (001) $SrTiO_3$ substrate are already crystallised at temperatures as low as 500–550°C. In addition the films are heteroepitaxied such as $(001)_{SBN}//(001)_{ST}$ and $[100]_{SBN}//[110]_{ST}$. Further experiments involving SBN or SBT deposition on $SrRuO_3$-coated, $SrTiO_3$ are now in progress.

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