

Chemical Solution Deposition of Oriented Ba₆Ti₂Nb₈O₃₀ Thin Films

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Thin films of tetragonal tungsten bronze type barium titanium niobate Ba₆Ti₂Nb₈O₃₀ (BTN) oriented to *c*-axis have first been grown on (100) SrTiO₃ substrates by metalorganic solution deposition (MOD) method. The sintering temperature for achieving single phase BTN can be lowered significantly in comparison with that for ceramic materials. The crystallographic in-plane orientation of the grown films is such that their *a*-axis is rotated by about $\pm 18.5^\circ$ with respect to that of the SrTiO₃ substrate. This rotation is closely associated with the presence of the rectangular frame formed by the meandering array of twelve oxygen octahedra peculiar to the unit cell of tetragonal tungsten bronze structure.

1. Introduction

Barium titanium niobate (Ba₆Ti₂Nb₈O₃₀, hereafter BTN) is a tetragonal ferroelectric material with tungsten bronze structure [1]. Its superior dielectric properties have first been found by Fang *et al.* [2]. An experiment on pulled single crystals of BTN has confirmed high spontaneous polarization and promising nonlinear optical properties [3]. It has also been observed that an appropriate addition of lanthanum to BTN ceramics improves the optical transparency of ceramic samples [4]. Recently, moreover, the demand for thin film process technologies of ferroelectrics has become more and more urgent from the point of view of ferroelectric nonvolatile memories [5].

Tungsten bronze materials can generally form cubic, tetragonal, hexagonal and their intergrowth structures depending on cation species. Tetragonal tungsten bronze structure is expressed by the general molecular formula of (A1)₂(A2)₄(C)₂(B1)₂(B2)₈O₃₀ and has a complex unit cell surrounded by meandering array of twelve oxygen octahedra [1]. Because of the complex atomic arrangement in the unit cell of tetragonal tungsten bronze structure, a rather high sintering temperature of 1250-1350°C is necessary for

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obtaining uniform single-phase ceramics of BTN in contrast with a much lower sintering temperature below 1000°C for perovskite ceramics.

A few studies on BTN have so far been done in bulk materials, single crystals [3] and ceramics [4]. However, thin films are inevitable for applications to nonlinear optical components and nonvolatile memories. In this article we describe the first successful attempt to synthesize *c*-axis oriented BTN thin films on (100) SrTiO₃ substrates by metalorganic deposition (MOD) method. It is demonstrated that the sintering temperature can be lowered down to 1000°C to obtain satisfactorily single phase BTN films aligned along *c*-axis. The crystallographic *a*-axis of the grown BTN films is rotated by about $\pm 18.5^\circ$ with respect to that of the (100) SrTiO₃ substrates. The reasonable origin of this crystallographic in-phase rotation is also discussed.

2. Experimental Procedures

The preparation of BTN films was carried out by MOD process using chemical solutions containing stoichiometric compositions of Ba, Ti and Nb. In order to avoid harmful influence of atmospheric moisture, necessary handling of the chemicals was conducted in dry N₂ atmosphere.

The stabilized solutions of Ba, Ti and Nb supplied commercially for MOD process (Kojundo Chemical Laboratory Co., Japan) were used. These solutions are originally provided for depositing BaO, TiO₂ and Nb₂O₅ oxide films, respectively. The precursor solution was made by mixing these solutions at the stoichiometric composition and by refluxing for several hours. The precursor solution was spin-coated on (100) SrTiO₃ substrates. The surface of the SrTiO₃ substrates was simply degreased with acetone ultrasonically without any special treatment. The spin-coated films were then dried and heated at 500 °C for 1 min in air. The coating-drying-heating process was repeated several times to increase the total thickness of the film. Finally the precursor films were fired in a flowing O₂ at various temperatures from 800 to 100 °C to crystallize into single phase BTN.

As another route to provide the precursor solution, barium di-*i*-propoxide [Ba(O-*i*-C₃H₇)₂], titanium tetra-methoxide [Ti(O-CH₃)₄] and niobium penta-*i*-propoxide [Nb(O-*i*-C₃H₇)₅] (Kojundo Chemical Laboratory Co., Japan) were used as the starting materials. The stoichiometric composition of the metalorganics, Ba(O-*i*-C₃H₇)₂, Ti(O-CH₃)₄ and Nb(O-*i*-C₃H₇)₅ were dissolved in 2-ethoxyethanol. Then the mixture solution was refluxed for 24 hours. The precursor solution thus prepared was employed to deposit BTN films by dip-coating-firing process on (100) MgO substrates and by

spin-coating-firing process on (100) SrTiO₃ and MgO substrates. Both MOD precursor solutions arranged in our laboratory from the constituent metalorganics and from the stoichiometric mixture of the commercially available constituent solutions yielded the c-axis oriented BTN films with essentially the same crystallographic characters. In this paper the results in the case of (100) SrTiO₃ substrates are mainly presented.

The orientation of the films normal to the substrate surface was characterized by X-ray θ - 2θ diffraction measurement (Rigaku, RAD2C). The in-plane alignment of the films with respect to the SrTiO₃ and MgO crystalline substrates was examined by pole figure (β -scan) analysis (Rigaku, RINT2000). The surface morphology of the films was observed by a scanning electron microscope (JEOL, JXA-8300R).

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the BTN films prepared by dip-coating on (100) MgO substrates and crystallized at various temperatures together with that for BTN powder sample (depicted as bulk). The film thickness was about 0.4 μm . For the films fired at 800 and 900 $^{\circ}\text{C}$ an intermediate phase indicated by the arrows is still observed because of insufficient sintering temperature in addition to the

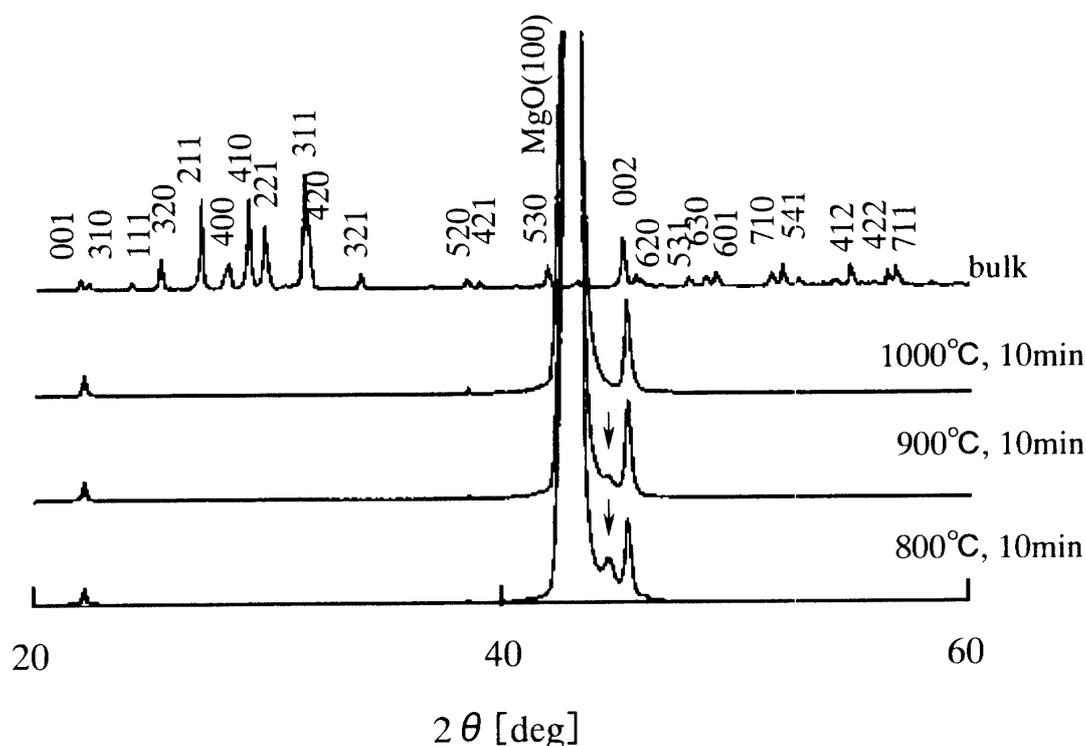


Figure 1. X-ray diffraction patterns of MOD films sintered at 800 - 1000 $^{\circ}\text{C}$ on (100) MgO substrate.

well-developed (001) and (002) reflections of BTN. The single phase BTN crystal is attained at the sintering temperature of 1000 °C. This sintering temperature is considerably reduced from that (1350 °C) required for preparing ceramic samples. However, the sintering temperature of 1000 °C is still higher than that for conventional perovskite ferroelectric films typically, for example, 700 °C or even less. The complex unit cell structure of tetragonal tungsten bronze ferroelectric materials and/or a relatively large thickness of the films is the possible reason for the higher sintering temperature.

The lattice constant of the *c*-axis is estimated to be 3.99 Å in Fig. 1, being slightly smaller than that of BTN powder (4.01 Å). This is considered to be due to an *a*-axis lattice mismatch between BTN (12.53 Å) and MgO (3*a*=12.61 Å) which can be accommodated by an elastic lattice dilatation in the *a*-plane accompanying a simultaneous change in the *c*-axis lattice constant. The half width of the (001) and (002) diffraction peaks is comparable to that of powder samples which are sintered at 1350 °C. This may suggest the existence of well-developed single crystalline regions, as was confirmed by the SEM observation.

In order to investigate the in-plane alignment of BTN films relative to the SrTiO₃ and MgO substrates, the X-ray pole figure measurement was carried out for

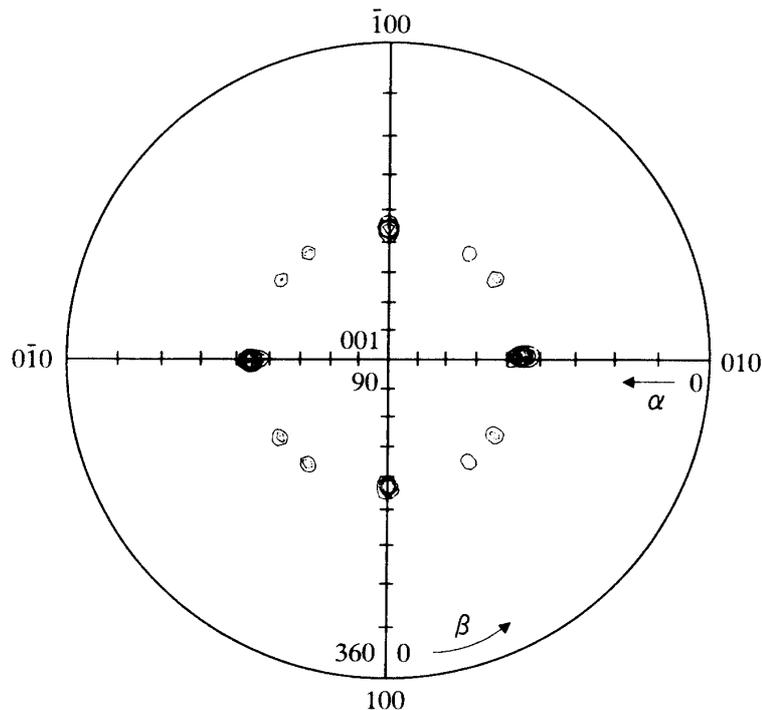


Figure 2. Pole figure pattern for the (311) plane of BTN film sintered at 1000 °C on (100) SrTiO₃ substrate.

(311) diffraction. The (311) plane was chosen because it has the highest diffraction intensity among a number of diffraction lines of BTN. Figure 2 shows a typical result of the pole figure pattern (β -scan) of the (311) plane of the BTN film sintered at 1000 °C on (100) SrTiO₃. Twelve spots are detected at the tilting angle α of 45° with intense four spots on the principal axes. The calculated diffraction spots from the (311) plane of tetragonal BTN ($a=12.53$ Å, $c=4.01$ Å) are eight in number as illustrated in Fig. 3. These eight spots are aligned symmetrically with respect to the four principal axes. It is reasonable to assume that the eight spots in Fig. 3 are split double into sixteen, eight of which happen to be overlapped into the intense four spots on the principal axes. This splitting of the diffraction spots is due to the rotation of the a -axis of the epitaxial BTN film with respect to that of the SrTiO₃ substrate. The rotation angle is estimated to be about $\pm 18.5^\circ$; this rotation angle is intimately related to the peculiar oxygen octahedra array in the unit cell of the tetragonal tungsten bronze structure. The essentially similar pole figure patterns were observed in BTN films on (100) MgO substrates, although there was a larger fluctuation of the diffraction spots.

The in-plane alignment of the a -axis of the deposited layer rotated by about $\pm 18.5^\circ$ with respect to that of the (100) substrate has also been observed in other

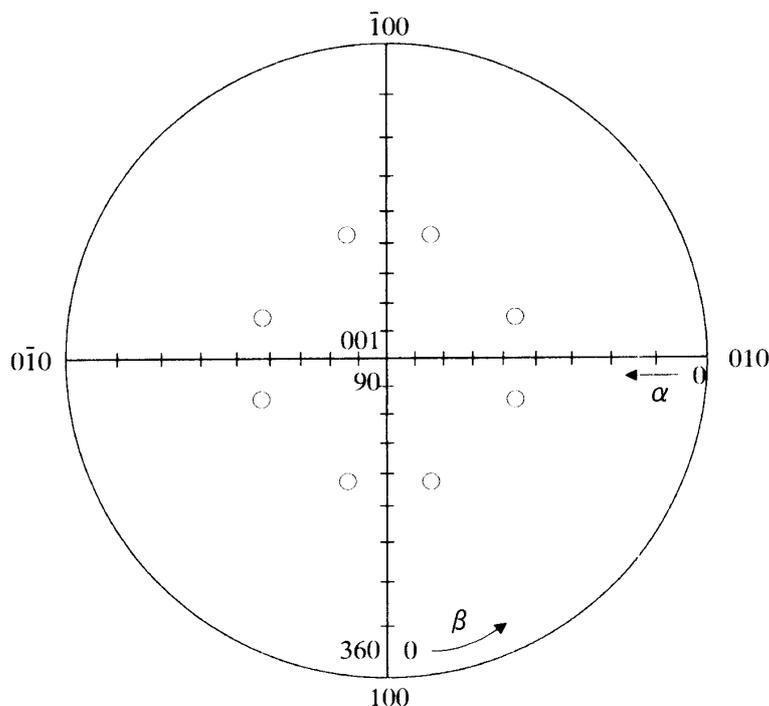


Figure 3. Theoretically predicted diffraction spots for the (311) plane of BTN tetragonal lattice.

tetragonal ferroelectric materials such as strontium barium niobate (SBN) grown on (100) MgO substrates [6,7]. The same thing has been found in the case of SBN deposited on (100) SrTiO₃ [8] and (100) Pt-coated MgO substrates [7]. These common phenomena reflect the peculiar arrangement of oxygen octahedra in a unit cell of tetragonal tungsten bronze type structure.

Figure 4 shows the cross-sectional view sectioned at $z=0$ of a unit cell of tetragonal tungsten bronze structure projected to the c -plane [1]. It should be pointed out here that the array of twelve oxygen octahedra, although they are slightly meandering, forms a nearing rectangular frame tilting by about 18° from the a -axis of the tetragonal lattice; this rectangular frame is associated with the commonly observed rotated nature of the in-plane alignment between the deposited layer and the (100) SrTiO₃ or (100) MgO substrate as has first been pointed out by Thöny et al. [6]. In the

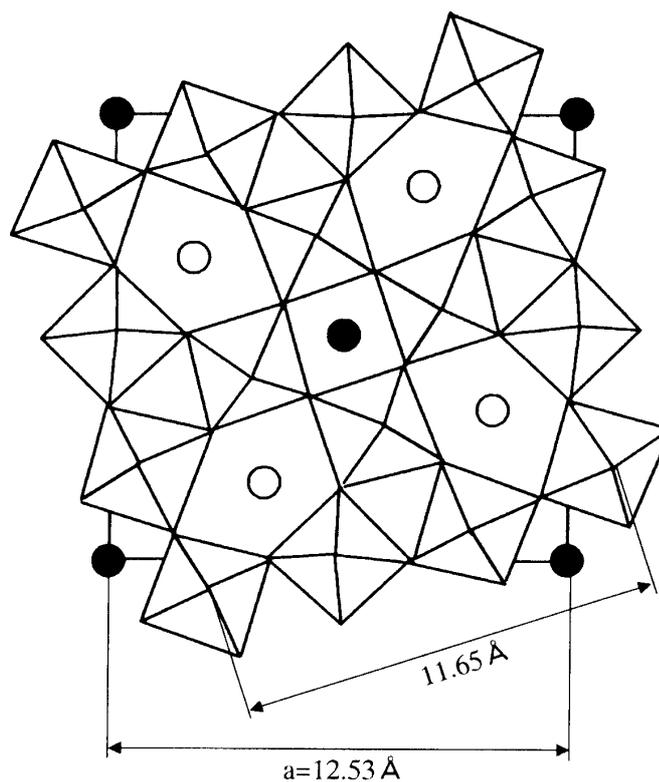


Figure 4. Plan view of a unit cell of tetragonal tungsten bronze structure. The solid and open circles indicate A_1 and A_2 sites, respectively. It is noted that twelve oxygen octahedra array forms a nearly rectangular frame which can grow epitaxially onto nine unit cells of SrTiO₃ or MgO substrate. The a -axis lattice constant and the size of the rectangular frame for BTN are 12.53 \AA and 11.65 \AA , respectively.

case of (100) SrTiO_3 substrate the size of the rectangular frame of BTN (11.65 Å) is almost equal to three times the lattice constant of SrTiO_3 (11.715 Å). On the other hand, the length of the meandering four octahedra array of BTN is smaller by about 7.5 % than three times the lattice constant of MgO (12.5308 Å). Although the mismatch of 7.5 % can be accommodated elastically by self-adjustment of the meandering four octahedra linear array, this large mismatch may be a reason for somewhat poor in-plane alignment and slight shrinkage in the c -axis lattice constant of the deposited films on (100) MgO substrates.

Thöny et al. [6] have discussed the epitaxial relationship at the interface between the deposited layer of SBT and the (100) MgO substrate. They conclude, in the aspect of electrostatic energy, that the first epitaxial layer prefers the $z=0$ plane of SBN where the center atoms of octahedra (Nb) are located. Since the crystal structure of MgO can be regarded as a layered structure with planar extension of edge-connected octahedra, it seems to be natural that the first epitaxial layer is the $z=0$ plane, of which

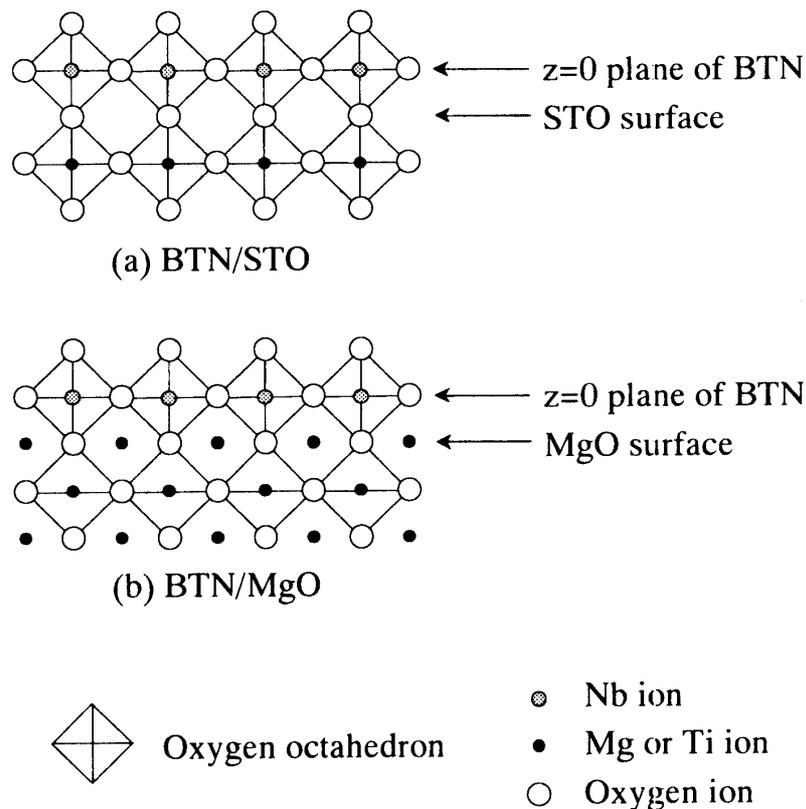


Figure 5. Side views of the atomic bondings at the interface between the first epitaxial layer of BTN and SrTiO_3 (a) and MgO (b) surfaces. Oxygen atoms on the $z=0$ plane of BTN bond tetrahedrally to oxygens on the SrTiO_3 or MgO surface to construct oxygen octahedra.

oxygen atoms bond to those at the MgO surface, resulting in forming oxygen octahedra. The same model of the atomic configuration at the interface holds more naturally in case of the SrTiO₃ substrate as illustrated in Fig. 5 (a). Figure 5 (b) depicts the side view of the atomic bondings at the interface between the rectangular frame of oxygen octahedra array in BTN crystal and the MgO substrate as has been discussed by Thöny et al. [6].

4. Summary

Metalorganic deposition of tetragonal ferroelectric BTN films has first been successfully carried out onto (100) SrTiO₃ and (100) MgO substrates. The single phase films oriented along the *c*-axis are obtained at the sintering temperature as low as 1000 °C which is remarkably improved in comparison with that for ceramic materials. It is found from the pole figure measurement that the unit cell of the deposited BTN films is rotated by about $\pm 18.5^\circ$ with respect to the (100) unit cell of the SrTiO₃ and MgO substrates. This rotation is due to the peculiar unit cell structure of the tetragonal tungsten bronze ferroelectrics in which a rectangular frame of oxygen octahedra arrays exists to match preferably nine unit cells of the cubic oxide substrates.

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