Epitaxial growth of high dielectric constant lead-free relaxor ferroelectric for high-temperature operational film capacitor

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Abstract

Epitaxial thin-film capacitor based on relaxor ferroelectric oxide, BaTiO₃-Bi(Mg_{2/3}Nb_{1/3})O₃ (BT-BMN), has been realized on Nb:SrTiO₃ substrates. A high dielectric constant exceeding 400 was attained on high-temperature annealed films at frequencies below 100 kHz. BT-BMN thin-film exhibited a broad dielectric constant variation against temperature and also the frequency dependent dielectric-constant-maximum temperature. Excellent dielectric constant stability below 10% was achieved in 75- 400 °C temperature range with a low dielectric loss. This exemplifies BT-BMN as a dielectric for monolithically integrated capacitors that can function up to 400 °C, breaking the present 175 °C limit of bulky capacitors, in high-power high-temperature electronic devices.

Keywords: relaxor ferroelectric, high dielectric constant, high-temperature operational capacitor, Pulsed laser deposition.

1. Introduction

High-frequency switchable high-power compact electronic devices that can function under high temperature harsh conditions are indispensable for aviation and automotive systems, smart power transmission, geothermal and space explorations and some domestic applications. A variety of wide-band gap semiconductor, such as SiC, GaN, and diamond, based high-power active devices have been developed over the years and are currently in advanced manufacturing stage[1,2,3,4]. These active devices are capable of operating at temperatures exceeding 250 °C and some of them demonstrated up to 500 °C [5,6]. In line with the progress in active devices development, it is also essential to develop compact passive components such as capacitors, resistors, inductors, and other package elements that are capable of handling high-powers and functional at elevated temperatures [7].

Capacitors are extensively used in power electronics as filters, coupler, electromagnetic interference (EMI) suppressor, snubber, sensors and smoothers etc. and are expected to withstand, like the active devices, up to 400 °C. However, at present, the maximum operating temperature of capacitors is 175 °C only. This shortcoming compels for an additional design and development of cooling systems in the power modules. Furthermore, these capacitors are bulkier and occupy a significant module space. Therefore, it is necessary to devise and develop capacitors that are compact in size and also functional up to 400 °C.

Thin-film capacitors that can be integrated monolithically with active device chip would be an attractive solution for compact module development. The key issues are i) identify a suitable dielectric medium for the capacitors and ii) development of thin-film process technology. The requisites for dielectrics are a material with high dielectric constant (over 300), high stability

of dielectric constant against temperatures at least up to 400°C and high-frequencies (1 MHz), high breakdown field, low dielectric loss, low leakage current, and free from hazardous elements such as the RoHS. Perovskite-structured materials especially, relaxor type ferroelectrics satisfy most of these criteria and can serve as an efficient dielectric for the capacitors [8,9]. Unlike normal ferroelectric materials, which exhibit a sharp variation of dielectric constant at phase transition temperatures, relaxors exhibit a broad peak associated with the random distribution of the so called polar nano regions (PNR). These thin film relaxors based high temperature operational film capacitors such as $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{--BaTiO}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ have been developed, exhibiting the high dielectric constant. However, lead (Pb) and sodium (Na) included in those relaxors are a hazardous element and a thermally unstable element, respectively [10,11]. To avoid these elements, a number of lead-free relaxor ferroelectric materials such as $\text{BiScO}_3\text{--Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ are explored for various electrical applications [8,12], however only a few systems are suitable for high-temperature capacitor applications. As a member of relaxor family, recently, $\text{BaTiO}_3\text{--Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ (BT-BMN) bulk ceramics showed a high dielectric constant and excellent stability of dielectric permittivity up to 400 °C [13]. This is very conspicuous for the development of high-temperature tolerant capacitors [14].

However, a thin-film process technology of this solid solution is not available and should be developed for monolithic integration of capacitors with other semiconductor devices. This will facilitate a compact power device with which, one can substantially reduce the parasitic inductance of connecting leads and wires, achieve high frequency switching and also take advantage of the high thermal conductivity of the SiC or diamond substrate to realize cooling-free efficient power modules. Among a numerous lead-free relaxor ferroelectric systems reported till date, a study on their epitaxial growth process is surprisingly very low [15,16,17]. A

capacitor composed of epitaxial dielectric film would show an enhanced performance because the grain boundary related leakage current can be suppressed, the polarization dependency on the crystallographic orientation can be controlled and importantly, the interfaces are clearly defined. Furthermore, one can expect an enormous increase of breakdown strength, as was reported in the Bi containing BaTiO_3 - BiScO_3 ceramics [18], when the thickness is reduced to few hundreds of nm. In this paper, we report the epitaxial growth of (111) oriented BT-BMN films on Nb doped (111) SrTiO_3 substrates by pulsed laser ablation (PLD) method, and demonstrate that this material has the potential to serve as a dielectric medium for high-temperature durable high-power integrated capacitors. From the point of view of the crystallographic structure compatibility with hexagonal SiC, the substrate orientation was chosen to be (111). The BT-BMN epitaxial film growth process is to be transferred eventually to hexagonal SiC based power devices for which, (111) oriented film would be structurally closer than conventional (001) films.

2. Experimental apparatus and method

Based on the temperature dependency of dielectric constant results of bulk ceramics [11], sintered ceramic target with a composition of $0.4[\text{BaTiO}_3]-0.6[\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3]$ enriched with Bi-10wt.% was prepared through solid state reaction route and preinstalled on the rotating stage of the deposition chamber. 0.5 wt.-%-Nb doped SrTiO_3 substrates cut and polished in (111) orientation were cleaned and loaded on the heating stage. A KrF excimer laser pulse of 248 nm wavelength with repetition rate of 10 Hz and energy density of 1.5 J/cm^2 was employed to ablate the target. The deposition was carried at several substrate temperatures chosen in the range of 490-580 °C. The growth atmosphere was oxygen and the partial pressure of oxygen was

set to 0.2, 2 or 20 Pa. After the deposition, the films were cooled down to room temperature under oxygen atmosphere. The thickness of the films was around 350 nm. Crystalline phase purity and epitaxial relationship of the films with the substrates were analyzed by x-ray diffraction (XRD) techniques using Bruker AXS D8 discover super speed with GADDS system equipped with a 5 kW rotating Cu anode and large area high-speed 2-D detectors. Rapid thermal annealing was carried out under 0.2 l/min. oxygen flow. Using a metal mask, circular Pt electrodes with 100 μm diameter and 125 nm thickness were deposited on the film by DC sputtering method. Similarly, a 125 nm thick film was deposited on the backside of SrTiO_3 to facilitate back contact. Current-voltage (I-V), capacitance-frequency (C-f) and capacitance-voltage (C-V) characteristics were measured, from room temperature to 400°C, using a source-measurement unit (Keithley, 2612B) and LCR meter (Agilent, E4980A) combination. The bias voltage was applied to the top electrode and the bottom electrode was grounded.

3. Results and Discussion

2D-XRD patterns of BT-BMN films grown on (111) substrates at temperatures 490 °C, 510 °C, and 530 °C, under an oxygen partial pressure of 20 Pa, are shown in Fig. 1(a). A clear singular diffraction corresponding to (111) reflection at 38.45° is seen for BT-BMN grown at 510 °C and 530 °C suggesting the high-crystalline orientation of the film. BT-BMN films deposited at 490 °C were polycrystalline as obvious from the Debye-Scherrer ring pattern. Here, (100) and (110) are the predominant planes indicating the ordering in those orientations is energetically favorable though it is on (111) oriented substrate. The diffraction pattern corresponding to the substrate is also seen in the pictures. Fig. 1(b) depicts the diffraction pattern

of BT-BMN films grown at the oxygen partial pressures of 20, 2 and 0.2 Pa with a fixed temperature of 510 °C that was also the optimal temperature. Except the film grown at 0.2 Pa, all other films were mono-crystalline. The full width at half maximum of chi (χ) angle of (111) reflection, which describes the mosaicity of the film, becomes narrower for 20 Pa grown film than others. To further investigate the details on the epitaxial relationship of the film with the substrates, pole figure measurements were carried out on the films deposited at 510 °C and 20 Pa. The d values corresponding to {110} and {211} reflections were chosen and the sample was rotated from 0° to 360° with tilts covering 20°- 50° range. As shown in Fig. 2, three sharp spots aligned around 34° and 18° corresponding to {110} and {211} reflections respectively. The absence of any stray pattern indicates the phase purity of the film. The spots corresponding to the film and the substrates are indicated in the enlarged version of the figure. The pole-figure results confirms the epitaxial relationship of BT-BMN film with Nb:SrTiO₃ substrate. The lattice spacing of the films is larger than that of the substrate as can also be seen from Fig. 1(a) and 1(b).

Figure 3(a) represents the dielectric constant as a function of frequency in the 1 kHz – 1 MHz range, derived from the frequency sweep of capacitance at 0 V bias, for BT-BMN films grown at 490 °C, 510 °C, and 530 °C with the oxygen partial pressure of 20 Pa. At any frequency, the dielectric constant is highest for BT-BMN film grown at 510 °C. It is lowest for the film deposited at 490 °C. It should be noted that the epitaxial relationship and crystalline phase purity are better for 510 °C deposited films. Figure 3(b) shows a C-V property of BT-BMN film grown at 510 °C. Capacitance increases slightly against the applied voltage less than 4 %, and did not show the ferroelectric behavior. Furthermore, all films showed similar trend (not shown). It is for this reason that C-f properties were mainly employed to determine the dielectric properties of BT-BMN films. To investigate the effect of heat treatment on the

electrical properties, the epitaxial films deposited at 20 Pa and 510 °C were chosen and annealed to high-temperatures, prior to electrode deposition, under an oxygen flow of 0.2 l/min. Fig. 3 compares the dielectric constant of the films in the as-grown state and after annealed at high temperatures. The film annealed at 775 °C showed higher dielectric constant than the as-grown film. It is further improved and a dielectric constant above 450 at 100 kHz was achieved for 850 °C annealed film. However, after the annealing at 900 °C, the degradations of **C-f** and surface morphology were observed. To understand the cause behind the improvement of dielectric constant, the annealed films were subjected to XRD analysis. When compared to as-grown state films, we could not observe any appreciable change in the 2D-XRD pattern and the crystal maintains its epitaxial relationship with the substrate. However, the mosaicity of 850 °C post-annealed film, grown at 510 °C – 20 Pa conditions, improved slightly as the FWHM of annealed film becomes 0.36° from 0.40° for as-grown film. This suggests that there is no crystal structure or phase distortion contribution to the dielectric constant enhancement. We believe the oxygen vacancy related defects play a major role in the enhancement of dielectric constant. Also, the Nb containing perovskite structured materials are known to tolerate a large number of vacancies [19]. The as-grown films are deficient of oxygen and high temperature annealing at oxygen atmosphere decreases the oxygen vacancy related defects. This causes the enhancement of dielectric constant because the cation positions in an ABO₃ type perovskite structure, responsible for the ferroelectric behavior [20], is altered in the presence or absence of oxygen vacancy [21]. Therefore, an optimal annealing temperature and time should be identified. For all the films, the dielectric constant decreases when the frequency is increased. The low frequency behavior of dielectric constant is typical of a capacitor and related to polarization response of the dielectric and interface to the varying electric field.

The dielectric constant of the films grown at 0.2, 2 and 20 Pa of oxygen partial pressures at a fixed temperature of 510 °C and post annealed at 850 °C is depicted in Fig. 4. The highest dielectric constant exceeding 400 was achieved on the films grown at 20 Pa and it is much higher than the as-grown state film. The dielectric constant of the films grown at low oxygen pressures are low and the crystalline quality is also inferior. The strong dependency of dielectric constant on the oxygen partial pressure further substantiates oxygen vacancy model discussed previously. The dielectric loss as a function of frequency is represented as dotted lines in Fig. 3 and Fig. 4. It slightly increases at higher frequencies. However, for all the films, the maximum dissipation is less than 0.2 for the entire frequency range.

The high-temperature **C-f** measurements were carried out on as-grown and 850 °C annealed films. The dielectric constant measured from room temperature to 400 °C, in the frequency range of 1 kHz to 1 MHz, at 0 V bias is shown in Fig. 5 for 850 °C post-annealed film. For clarity, the dielectric constant estimated at 100 KHz alone is presented for the as-deposited film. The dielectric constant is nearly flat at low temperature region and increases at the high temperature end. The dielectric constant of annealed film increases initially with the rise of temperature and showed a plateau and later a decreasing tendency. A clear frequency dispersion of dielectric constant, typical of a relaxor ferroelectric nature is observed in the low temperature regime. The highest dielectric constant exceeding 400 was obtained, at frequencies below 100 kHz, for 850 °C annealed film. As a dielectric material, BT-BMN is capable of withstanding up to 400°C with a high dielectric constant. For the as-grown film, the dielectric loss increases in the high temperature region. In contrast, the 850°C annealed film showed lower dielectric losses even at 400°C. The low dielectric loss is attributed to the oxygen vacancy related defect reduction after 850 °C oxygen annealing. The dielectric constant stability of the film against

temperature is defined as $\frac{\Delta C}{C} = \frac{\epsilon_{max} - \epsilon_{min}}{\epsilon_{RT}} \times 100 \%$ where, ϵ_{max} , ϵ_{min} and ϵ_{RT} are respectively the maximum, minimum and room temperature dielectric constants. This value is below 10% for the 850 °C annealed film in the temperature range of 75 °C- 400 °C at frequencies below 100 kHz. Here, the dielectric constant also exceeds 500. A large variation of the dielectric constant occurs at low temperatures (<125 °C) that corresponds to the phase transition temperature of BaTiO₃. This could be reduced further through a composition and stoichiometry control of the film [11].

PLD is known as a process that transforms the target composition into a film. However, still there are some shortcomings that argue for inconsistency of film stoichiometry. In complex oxide systems, this off-stoichiometry of the film is attributed to the deposition of incongruent ablated species and preferential scattering of lighter atoms in an oxygen atmosphere [22]. The laser fluence is also affecting the growth front in Ti containing oxides [23,24]. Considering the above facts and high volatility of Bi, especially, in solid solutions like BaTiO₃-Bi(Mg_{2/3}Nb_{1/3})O₃ the stoichiometry of the films is expected to be deviated from the target composition. Besides the stoichiometry related issues, other substrate effects related to film growth may affect the dielectric properties and its stability against temperature. Even though the substrate clamping effect is relatively small in (111) orientation of Bi containing ferroelectric compounds [25], a complete elimination of clamping effect of the substrates [26] and misfit strain [27] predicted in relaxor films cannot be ruled out. Their influence on the dielectric properties of BT-BMN is not investigated yet. To improve the film stoichiometry, the target composition should be enriched with an appropriate Bi concentration to compensate the volatility of Bi. By optimizing the growth conditions and with appropriate electrodes structures, it is possible to improve the dielectric constant value of BT-BMN and the dielectric constant stability further. Nevertheless, a high dielectric constant exceeding 500 together with a high-temperature stability below 10% (75-

400 °C range) at frequencies below 100 kHz, achieved in this investigation, is still attractive for high-temperature capacitor dielectrics when compared to other lead-free relaxor systems [14,28,29].

4. Conclusions

An epitaxial thin-film processing technology has been developed for the lead-free BT-BMN complex oxide ceramics. This will open up the monolithic fabrication of capacitor with other active devices. The films grown at 510 °C and 20 Pa showed the highest crystalline order that also offered a high dielectric constant in the as-grown state. Post growth annealing significantly increased the dielectric constant and oxygen vacancy related defects found to play a crucial role on the electrical properties of the film. A high dielectric constant stability of 10% together with a high dielectric constant exceeding 500 was achieved in the 75-400 °C temperature range with low dielectric loss. This facilitates the availability of monolithic capacitors that functions up to 400 °C well-surpassing the present limitation of 175 °C temperature limit.

Acknowledgements

Funding from Japan Science and Technology Agency (JST) - Adaptable & Seamless Technology Transfer Program through Target-driven R&D (A-STEP, No. AS2315002B) and World Premier International Research Center Initiative Program of MEXT is gratefully acknowledged.

Figure Captions

Fig. 1. Two dimensional x-ray diffraction patterns of BT-BMN films deposited on (111) SrTiO_3 substrates (a) at different substrate temperatures of 490 °C, 510 °C and 530 °C with a fixed oxygen partial pressure of 20 Pa and (b) at 20, 2 and 0.2Pa with a fixed temperature of 510 °C.

Fig. 2. Pole figure showing 3 fold symmetry of {110} and {211} reflections projected on (111) plane confirming the epitaxial relation of the out-of-plane film with the in-plane substrate. The spot positions calculated for {110} and {211} reflections are shown on the right. The diffraction spots related to film and substrates are indicated in the magnified picture (bottom).

Fig. 3. (a) Dielectric constant (solid lines) and dielectric loss (dotted lines) of the films, deposited at temperatures 490 °C, 510 °C and 530 °C on (111) oriented substrates at 20 Pa, and post annealed at 775 °C, 825 °C, 850 °C, and 900 °C, as a function of sweep frequency. (b) C-V property of the film deposited at 510 °C.

Fig. 4. Frequency dispersion of dielectric constant (solid lines) and loss (dotted lines) of films grown at 0.2, 2, and 20 Pa at a fixed temperature of 510 °C and post annealed at 850 °C.

Fig. 5. High-temperature characteristics of dielectric constant (lines with symbol) and dielectric loss (lines only) of as-grown (100 kHz) and 850 °C post-growth annealed (1 kHz – 1 MHz) films measured at 0 V bias.

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Fig. 2. Kumaragurubaran, et. al.

Figure 3

Fig. 4. Kumaragurubaran, et. al.

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