Thermally stable dielectric responses in uniaxially (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ nanofilms grown on a Ca$_2$Nb$_3$O$_{10}^-$ nanosheet seed layer

Junichi Kimura$^1$, Itaru Takuwa$^1$, Masaaki Matsushima$^1$, Takaao Shimizu$^1$, Hiroshi Uchida$^3$, Takanori Kiguchi$^4$, Takahisa Shiraishi$^4$, Toyohiko J. Konno$^4$, Tatsuio Shibata$^5$, Minoru Osada$^5$, Takayoshi Sasaki$^5$ & Hiroshi Funakubo$^{1,2}$

To realize a high-temperature capacitor, uniaxially (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ films with various film thicknesses were prepared on (100),SrRuO$_3$/Ca$_2$Nb$_3$O$_{10}^-$ nanosheet/glass substrates. As the film thickness decreases to 50 nm, the out-of-plane lattice parameters decrease while the in-plane lattice ones increase due to the in-plane tensile strain. However, the relative dielectric constant ($\varepsilon_r$) at room temperature exhibits a negligible degradation as the film thickness decreases to 50 nm, suggesting that $\varepsilon_r$ of (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ is less sensitive to the residual strain. The capacitance density increases monotonously with decreasing film thickness, reaching a value of 4.5 $\mu$F/cm$^2$ for a 50-nm-thick nanofilm, and is stable against temperature changes from room temperature to 400 °C irrespective of film thickness. This behaviour differs from that of the widely investigated perovskite-structured dielectrics. These results show that (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ films derived using Ca$_2$Nb$_3$O$_{10}^-$ nanosheets as seed layers can be made candidates for high-temperature capacitor applications by a small change in the dielectric properties against film thickness and temperature variations.

The demand is increasing for capacitors that can function at elevated temperatures in electronic circuits in automobiles, power devices, and light-emitting diodes$^{1-4}$. One of the most promising candidates is a ceramic capacitor due to its thermal stability. Recently, various approaches have been used to improve the performance of ceramic capacitors, including the preparation of thin-film capacitors composed of inorganic dielectrics such as perovskite-structured oxides. Although (Ba, Sr)TiO$_3$-based dielectrics, which have a high dielectric constant ($\varepsilon_r$) near room temperature, are the most widely investigated ceramic capacitor materials$^{5-7}$, they are not suitable for high-temperature capacitor applications due to their temperature instability within the required temperature range (i.e., $\varepsilon_r$ changes drastically around the phase transition temperature). Consequently, they cannot achieve high $\varepsilon_r$ and a small-temperature dependence of the capacitance simultaneously due to the trade-off relationship$^{57}$.

In addition, the $\varepsilon_r$ of thin-film capacitors produced using (Ba, Sr)TiO$_3$-based materials as the dielectric layer is severely degraded as the film thickness decreases, making it difficult to enhance the capacitance density by decreasing the film thickness$^{8-10}$. One possible reason for this sensitivity to film thickness may be the high strain sensitivity of $\varepsilon_r$, which remains as the film thickness decreases. These phenomena are common material problems for conventional perovskite dielectrics, suggesting that another novel capacitor material is necessary.

1Department of Innovative and Engineered Materials, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midoriku, Yokohama, Kanagawa 226-8502, Japan. 2Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan. 3Department of Materials and Life Science, Sophia University, Chiyoda, Tokyo, 102-8554, Japan. 4Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan. 5International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan. Correspondence and requests for materials should be addressed to H.F. (email: funakubo.h.aa@m.titech.ac.jp)
To realize novel dielectrics with a large capacitance density and small change in $\varepsilon_r$ at elevated temperatures, we previously proposed bismuth layer-structured dielectrics (BLSDs)\textsuperscript{11}. BLSDs have a natural superlattice structure along the $c$-axis [(001)-orientation], which consists of two kinds of two-dimensional monolayers (i.e., a bismuth oxide (Bi$_2$O$_2$)$_2^+$ layer and a pseudoperovskite layer generally described as (A$_{m-1}$B$_m$O$_{3m+1}$)$^2^−$, where $m$ is the number of BO$_6$ octahedra in the pseudoperovskite layer)\textsuperscript{12,13}. Compared to BaTiO$_3$-based materials, some BLSDs exhibit a high Curie temperature and their $\varepsilon_r$ shows small temperature dependence along the stack direction (i.e., the $c$-axis) up to the high temperature region\textsuperscript{14–16}. These materials also have important additional features in which the degradation in $\varepsilon_r$ as the film thickness decreases is small (i.e., a small "size effect"), allowing a high capacitance density to be realized\textsuperscript{17}. This behaviour showing the small strain sensitivity of $\varepsilon_r$, which is attributed to the structural two-dimensionality of BLSDs, differs from conventional perovskite-based dielectrics.

We have already investigated the dielectric properties of 500-nm-thick (001)-oriented epitaxial films of CaBi$_4$Ti$_4$O$_{15}$, which are BLSDs prepared on (100)SrRuO$_3$/SrTiO$_3$. These films not only have an $\varepsilon_r$ of about 190 at room temperature, but they also display a stable capacitance against the applied electric field as well as temperature variations up to 500 °C\textsuperscript{11}. Moreover, the $\varepsilon_r$ for epitaxial thin films of SrBi$_4$Ti$_4$O$_{15}$ is another BLSD, does not drastically degrade as the film thickness decreases to 15 nm\textsuperscript{17}. These reports clearly show that the $\varepsilon_r$ of thin-film capacitors of epitaxial BLSDs have a superior temperature-dependent performance compared to BaTiO$_3$-based ones and may overcome issues observed in conventional BaTiO$_3$-based materials in high-temperature applications.

However, the dielectric properties of BLSDs include a strong anisotropy due to the crystal structure of BLSDs\textsuperscript{16}. In fact, our group has previously reported that the dependence of the film thickness on the dielectric property in BLSDs is strongly influenced by the tilting angle of the $c$-axis from the substrate normal\textsuperscript{18}. Therefore, reproducible growth of (001)-oriented BLSDs films (i.e., the stack direction of the layers) is a critical issue to achieve a stable $\varepsilon_r$ as both the film thickness and temperature decrease.

From the viewpoint of practical applications, reproducible fabrication of uniaxially (001)-oriented BLSDs films on various common substrates, including amorphous glasses and (100) Si wafers, is a critical issue for practical applications even if the in-plane orientation of these films is more random than that of epitaxial films. Shibata \textit{et al.} reported the [100] orientation control of SrTiO$_3$ films on amorphous glass using a seed layer of Ca$_2$Nb$_3$O$_{10}$ nanosheets\textsuperscript{19}. Based on their work, we envisioned that a Ca$_2$Nb$_3$O$_{10}$ seed layer could control the (001) orientation of BLSD films because (001)-oriented BLSD films were grown on (100)SrTiO$_3$ single crystals\textsuperscript{19}.

In the present study, we sought to enhance the capacitance density of Pt/(001)-oriented CaBi$_4$Ti$_4$O$_{15}$(100)SrRuO$_3$ capacitors by decreasing the film thickness of the CaBi$_4$Ti$_4$O$_{15}$ layer. This should allow the capacitor size to be scaled down or the total capacitance to be increased. In the case of (Ba, Sr)TiO$_3$ film capacitors, $\varepsilon_r$ is reported to change drastically not only with film thickness but also with temperature, which makes it difficult to design a capacitor with a small capacitance change over a wide temperature range\textsuperscript{4–10}. For (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ films, the capacitance density reaches 4.5 $\mu$F/cm$^2$ as the film thickness is decreased to 50 nm, and the capacitance has a small temperature coefficient from room temperature to 400 °C despite the increase in the residual strain.
as the film thickness decreases. The present results indicate that nanosheet-buffered uniaxially (001)-oriented CaBi\(_4\)Ti\(_4\)O\(_{15}\) thin films are promising alternatives to (Ba, Sr)TiO\(_3\)-based films in high temperature capacitors.

**Results and discussion**

**Crystal structure and microstructure.** The out-of-plane XRD \(\theta-2\theta\) patterns for CaBi\(_4\)Ti\(_4\)O\(_{15}\) films with various thicknesses show only the (00\(l\)) and (00\(l\)) diffraction peaks of SrRuO\(_3\) and CaBi\(_4\)Ti\(_4\)O\(_{15}\) (Fig. 1(a)), respectively, suggesting a (001) single orientation of CaBi\(_4\)Ti\(_4\)O\(_{15}\) regardless of the film thickness. The X-ray pole figure measurement at a fixed \(2\theta\) angle corresponding to CaBi\(_4\)Ti\(_4\)O\(_{15}\) (00\(l\)) \((2\theta = 30.6^\circ)\) shows strong ring-shape-peaks at \(\Psi \approx 50^\circ\) for 780-nm-thick films (inset of Fig. 1(a)), indicating a uniaxial (001)-orientation along the substrate surface normal with an in-plane random orientation.

Figure 1(b) presents the enlarged XRD patterns around the CaBi\(_4\)Ti\(_4\)O\(_{15}\) (00\(l\)) peak shown in Fig. 1(a). The diffraction angles of the CaBi\(_4\)Ti\(_4\)O\(_{15}\) (00\(l\)) peak become higher as the film thickness decreases, indicating that the \(c\)-axis lattice parameters along the substrate normal decrease. Moreover, the in-plane XRD patterns around CaBi\(_4\)Ti\(_4\)O\(_{15}\) 220 are shown in Fig. 1(c). The CaBi\(_4\)Ti\(_4\)O\(_{15}\) 220 peaks shift toward a lower diffraction angle with decreasing film thickness, suggesting an increase in the in-plane lattice parameter (i.e., the \(a\)-axis).

Figure 2(a,b) plot the out-of-plane \(c\)-axis and in-plane \(a\)-axis lattice parameters calculated from the diffraction data shown in Fig. 1(a–c) as functions of film thickness, respectively. Additionally, reference data for the CaBi\(_4\)Ti\(_4\)O\(_{15}\) powder are shown. The in-plane XRD measurements confirm that clear peak splitting is not detected for the 200/020 peak irrespective of the film thickness because the lattice parameters of the \(a\)- and \(b\)-axes are very close in the CaBi\(_4\)Ti\(_4\)O\(_{15}\) crystal lattice (data not shown). The out-of-plane and in-plane lattice parameters for the 780-nm-thick film are almost the same as the reported data for strain-free CaBi\(_4\)Ti\(_4\)O\(_{15}\) powder. As the film thickness decreases, the out-of-plane \(c\)-axis lattice parameter decreases and drops drastically below 200 nm, whereas the in-plane \(a\)-axis and \(b\)-axis lattice parameters increase from 5.42 to 5.46 Å.

To analyse the change in the lattice parameter of CaBi\(_4\)Ti\(_4\)O\(_{15}\) films, Fig. 2(b) also plots the in-plane lattice parameter of the underlying SrRuO\(_3\) bottom electrodes obtained from Fig. 1(c) as well as the in-plane lattice parameter of the as-deposited SrRuO\(_3\) layer before CaBi\(_4\)Ti\(_4\)O\(_{15}\) film deposition along with the reference data of Ca\(_2\)Nb\(_3\)O\(_{10}\). The in-plane lattice parameter of CaBi\(_4\)Ti\(_4\)O\(_{15}\) for a 780-nm-thick film is almost equivalent to
that of the CaBi$_4$Ti$_4$O$_{15}$ powder, suggesting that the crystal lattice of the 780-nm-thick CaBi$_4$Ti$_4$O$_{15}$ film is almost relaxed. Meanwhile, the in-plane lattice parameter of CaBi$_4$Ti$_4$O$_{15}$ increases as the film thickness decreases. A similar trend is observed for the in-plane lattice parameters of SrRuO$_3$. It should be noted that the in-plane lattice parameter of SrRuO$_3$ is almost identical to that of the as-deposited 50-nm-thick SrRuO$_3$ films before CaBi$_4$Ti$_4$O$_{15}$ deposition but not to that of the Ca$_2$Nb$_3$O$_{10}$$^-$$^-$ nanosheets (Fig. 2(b)) because the crystal lattice of the as-deposited SrRuO$_3$ layer is not fully clamped on the lattice of the Ca$_2$Nb$_3$O$_{10}$$^-$ nanosheets. CaBi$_4$Ti$_4$O$_{15}$ also possesses a different in-plane lattice parameter from those of the SrRuO$_3$ and Ca$_2$Nb$_3$O$_{10}$ nanosheets, indicating that the change in the lattice parameter of CaBi$_4$Ti$_4$O$_{15}$ films is not perfectly clamped by the crystal lattice of the underlying SrRuO$_3$ electrode layer. The increase in the in-plane lattice parameter of the CaBi$_4$Ti$_4$O$_{15}$ film (Fig. 2(b)) suggests that the in-plane residual strain of CaBi$_4$Ti$_4$O$_{15}$ films increases as the film thickness decreases. The large in-plane lattice parameter of thin CaBi$_4$Ti$_4$O$_{15}$ is considered to be a response to the larger lattice parameter of the underlying SrRuO$_3$ layer, because the CaBi$_4$Ti$_4$O$_{15}$ films are thinner than the 50 nm-thick SrRuO$_3$ layer. Here, as-deposited SrRuO$_3$ films have a larger unit cell than SrRuO$_3$ powders, i.e., a larger in-plane strain, due to the damage occurring under the sputtering process using the present deposition conditions, as reported previously$^{21,22}$. The in-plane lattice parameter of CaBi$_4$Ti$_4$O$_{15}$, relaxed and approached the bulk value together with the SrRuO$_3$ layer with the increase in the total thickness.

Figure 3(a,b) shows atomic force microscopy (AFM) topographic images of Ca$_2$Nb$_3$O$_{10}$ nanosheets on glass substrates and CaBi$_4$Ti$_4$O$_{15}$ films, together with (c) cross sectional low-angle annular dark field-scanning transmission electron microscope (LAADF-STEM) images of the films.

**Dielectric property.** Figure 4(a) shows the $\varepsilon_r$ for the (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ films measured at room temperature and 100 kHz as functions of the film thickness. The $\varepsilon_r$ of these films is approximately 210, which is a negligible degradation as the film thickness decreases to 50 nm. This is almost equivalent to the results for epitaxial films$^{17}$. As a reference of $\varepsilon_r$, the $\varepsilon_r$ values for (Ba$_{0.7}$Sr$_{0.3}$)$_2$TiO$_3$ films reported by Parker et al., which continuously degrade as the film thickness decreases below 600 nm, are also plotted in Fig. 4(a)$^9$. The $\varepsilon_r$ value of (Ba$_{0.7}$Sr$_{0.3}$)$_2$TiO$_3$ films becomes smaller than that of CaBi$_4$Ti$_4$O$_{15}$ with a film thickness below 80 nm, suggesting that a
CaBi$_4$Ti$_4$O$_{15}$ layer less than 80-nm thick achieves a thin-film capacitor with a higher capacitance density than the conventional (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ one.

Figure 4(b) shows the capacitance density at room temperature as a function of film thickness, where the dashed line indicates the estimated data assuming that the CaBi$_4$Ti$_4$O$_{15}$ film has an almost constant $\varepsilon_r$ value ($\varepsilon_r = 210$, which is equivalent with that of the 780-nm-thick specimen) as the film thickness changes. The theoretical capacitance density is generally proportional to the inverse of the film thickness. The capacitance densities of the obtained (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ films are almost identical to the estimated values. As the film thickness decreases, the density increases and reaches a value of 4.5 $\mu$F/cm$^2$ at a thickness of 50 nm.

It is noteworthy that $\varepsilon_r$ remains almost constant despite the increase in the residual strain as the thickness is scaled down to 50-nm (Fig. 2). Thus, we confirm that $\varepsilon_r$ of the (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ films is free from the size-effect of the capacitance. This is an important feature not only for epitaxial (001)-oriented BLSD films, as already mentioned, but also for uniaxially (001)-oriented ones.

Figure 5 shows the frequency dependencies of the capacitance density and dielectric loss, tan $\delta$, measured from room temperature to 400 °C for 70 and 140 nm-thick CaBi$_4$Ti$_4$O$_{15}$ films. The capacitance density is almost independent of the measurement frequency from 100 to 10 kHz irrespective of the measurement temperature up to 400 °C. On the other hand, tan $\delta$ decreases with increasing measurement frequency from 100 to 10 kHz, but increases again above 10 kHz for 70 nm thick films as shown in Fig. 5(a). The relatively large dielectric loss at low frequency may originate from the leakage of the capacitor. The tan $\delta$ value increases as the measurement temperature increases due to the contribution from leakage current. However, the tan $\delta$ of 140 nm thick films remains at a low value below 4%, almost independent of the frequency from 10 to 10 kHz, even at the highest measurement temperature of 400 °C, as shown in Fig. 5.

It must be mentioned that no noticeable peel-off of CaBi$_4$Ti$_4$O$_{15}$ films was detected, either in the case of as-deposited films or in the case of films at the highest measurement temperatures of up to 400 °C irrespective of the film thickness.

Figure 6 plots the temperature dependence of the capacitance density and tan $\delta$ for (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ films with different thicknesses. The capacitance density of these films has a negative slope versus temperature, but shows a small temperature coefficient of capacitance ($TCC$, $TCC \equiv \frac{\Delta C}{C_{(R, T)}} \cdot \frac{1}{\Delta T}$), which is based on the defini-
Figure 5. Frequency dependencies of the capacitance density and dielectric loss, tan δ, measured from room temperature to 400 °C for (a) 70 and (b) 140 nm-thick CaBi$_4$Ti$_4$O$_{15}$ films.

Figure 6. Capacitance density (a) and dielectric loss (tan δ) (b) of the films as a function of temperature.
tion of the Electronic Industries Alliance) in the temperature range from 25 to 400 °C regardless of film thickness down to 50 nm. These TCC values fall within the range from −350 to −120 ppm/°C; this characteristic is almost equivalent to that of the epitaxial films in our previous work. These results imply that uniaxially (001)-oriented CaBi₄Ti₄O₁₅ films with an in-plane random crystal orientation have dielectric and insulating properties with a small temperature dependence similar to epitaxial films. The capacitance density increases with decreasing film thickness for all temperature regions (Fig. 6(a)). On the other hand, the tan δ value increases with the temperature due to the increase of the leakage current, as shown in Fig. 6(b). However, it decreases with increasing film thickness, especially if it is below 10% up to 400 °C for the films above 100 nm in thickness.

To analyse the effect of thickness on the capacitance density at elevated temperatures, Fig. 7(a) compares the capacitance densities for (001)-oriented CaBi₄Ti₄O₁₅ films measured between 150 °C and room temperature. The dashed line indicates the case without a degraded capacitance density up to 150 °C. The measured data are almost located on the dashed line, indicating a negligible difference in the capacitance change between these two temperatures. Figure 7(a) also plots the data for (Ba₀.₇Sr₀.₃)TiO₃ films as a reference; as the temperature increases to 150 °C, the capacitance density for thicker films drastically decreases and has a negative TCC value. In addition, Fig. 7(b) compares the capacitance densities at 400°C and room temperature. The measured data are also located for (001)-oriented CaBi₄Ti₄O₁₅ films on the dashed line even at temperatures as high as 400 °C. The estimated degradations of the capacitance density from room temperature to 150 and 400 °C are 7% and 9% for 50-nm-thick CaBi₄Ti₄O₁₅ films, respectively. Unlike conventionally investigated (Ba₀.₇Sr₀.₃)TiO₃ films where the capacitance decreases to 55% between room temperature and 150 °C, the capacitance density for uniaxially (001)-oriented CaBi₄Ti₄O₁₅ films shows a small degradation as the temperature increases to 400 °C. These results suggest that (001)-oriented CaBi₄Ti₄O₁₅ films produced using Ca₂Nb₃O₁₀ nanosheet seed layers are novel candidates for high-temperature adaptive capacitor applications due to the superior temperature stability of their electric properties up to 400 °C along with their high capacitance density, which is derived from the small "size effect" upon scaling down the film thickness.

Summary. Uniaxially (001)-oriented CaBi₄Ti₄O₁₅ films with various film thicknesses were prepared on (100),SrRuO₃/Ca₂Nb₃O₁₀ nanosheets/glass substrates. All films exhibited a (001) single orientation along the substrate surface normal, but had a random in-plane orientation. The continuous increase in the residual tensile strain as the film thickness decreases leads to a reduction in the out-of-plane "c-axis" lattice parameters and an increase in the in-plane "a- and b-axes" ones. However, the change in εᵣ is unremarkable as the film thickness decreases to 50 nm. Consequently, the monotonous increase in the capacitance density is proportional...
Methods

Uniaxially (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ films with various film thicknesses were prepared on (100) SrRuO$_3$/(Ca$_2$Nb$_3$O$_{10}$) nanosheets/glass substrates. The CaBi$_4$Ti$_4$O$_{15}$ and about 50 nm-thick SrRuO$_3$ layers were fabricated on (Ca$_2$Nb$_3$O$_{10}$) nanosheets/glass (Corning®1737) by the RF-magnetron sputtering method at substrate temperatures of 600 and 550 °C, respectively. The 1–2 unit-thick Ca$_2$Nb$_3$O$_{10}$ nanosheet layers were coated onto glass substrates by the Langmuir-Blodgett process$^{26,24,25}$. We chose CaBi$_4$Ti$_4$O$_{15}$ as the dielectric layer because its high Curie temperature of 790 °C enables a small temperature dependence of the capacitance at elevated temperatures. The deposition time controlled the CaBi$_4$Ti$_4$O$_{15}$ film thickness between 50 and 780 nm. Details of the deposition are described elsewhere$^{11}$. After preparing circular Pt top electrodes (100 μm in diameter) by electron-beam deposition, the Pt/CaBi$_4$Ti$_4$O$_{15}$/SrRuO$_3$ capacitors were annealed at 400 °C for 30 min under O$_2$ gas flow.

The constituent phase and crystal orientation of the deposited films were identified by X-ray diffraction (XRD) using a Philips X’pert MRD with Cu Kα radiation. The residual strain state was also estimated as in-plane XRD measurements using a Rigaku Smart-lab diffractometer with Cu Kα radiation. The electrical properties under various temperatures were measured using an impedance analyser (HP4194A, Agilent) and a sample-heating high-temperature capacitor applications.

Acknowledgements

This work was partially funded by the MEXT Elements Strategy Initiative to Form Core Research Center. This work was partially supported by the Center for Integrated Nanotechnology Support at Tohoku University and the Nanotechnology Network Project of MEXT of the Japanese Government. The authors thank Ms. Yumiko Kodama and Kumiko Suzuki for preparing the samples in the microstructure analysis.

References

1. Nishikawa, J., Hagiwara, T., Kobayashi, K., Mizuno, Y. & Kishi, H. Effect of microstructure on the Curie temperature in BaTiO$_3$-Ho$_2$O$_3$-Mg$_2$SiO$_4$. *Ipn. J. Appl. Phys.* 46, 6999–7004 (2007).
2. Simon, P. & Gogot’yi, Y. Materials for electrochemical capacitors. *Nature Mater.* 7, 845–854 (2008).
3. Simon, P. & Gogot’yi, Y. Capacitive energy storage in nanostructured carbon–electrolyte systems. *Acc. Chem. Res.* 46, 1094–1103 (2013).
4. Almeida, P. S., Soares, G. M., Pinto, D. & Braga, H. A. C. Integrated SEPIC buck-boost converter as an off-line LED driver without electrolytic capacitors. *Proc. IEEE 2012*, 4551–4556 (2012).
5. Smolenskii, G. A. & Rongachev, K. I. Dielectric properties of solid solutions in the system of barium titanate–strontium titanate. *Zh. Tekh. Fiz.* 24, 1751–1760 (1954).
6. Kang, D.-S., Han, M.-S., Lee, S.-G., Song, S.-H. Dielectric and pyroelectric properties of barium strontium calcium titanate ceramics. *J. Eur. Ceram. Soc.* 23, 515–518 (2003).
7. Cockbain, A. G. & Harrop, P. J. The temperature coefficient of capacitance. *J. Phys. D: Appl. Phys.* 1, 1109–1115 (1968).
8. Huang, Y.-L., Lee, Y.-C., Tsai, D.-C., Yeh, Y.-Y. & Shieu, F.-S. A. Study of low-temperature sintering of (Ba$_{0.6}$Sr$_{0.4}$)(Ti$_{0.94}$Cu$_{0.06}$)O$_3$ ceramics with B$_2$O$_3$ addition. *Ferroelectrics* 434, 147–156 (2012).
9. Parker, C. B., Maria, J.-P. & Kingon, A. I. Temperature and thickness dependent permittivity of (Ba, Sr)TiO$_3$ thin films. *Appl. Phys. Lett.* 81, 340–342 (2002).
10. Lee, B. T. & Hwang, C. S. Influences of internal intrinsic low-dielectric layers on the dielectric properties of sputtered (Ba, Sr)TiO$_3$ thin films. *Appl. Phys. Lett.* 77, 124–126 (2000).
11. Kimura, J. et al. Temperature and electric field stabilities of dielectric and insulating properties for c-axis-oriented CaBi$_4$Ti$_4$O$_{15}$ films. *J. Appl. Phys.* 114, 027002–1–027002–7 (2013).
12. Aurivillius, B. Mixed bismuth oxides with layer lattice. I. The structure type of Ca$_2$Nb$_3$O$_{10}$. *Ark. Kemi.* 1, 463–480 (1949).
13. Aurivillius, B. Mixed Bismuth oxides with layer lattice. I. The structure type of Bi$_2$Ti$_3$O$_{10}$. *Ark. Kemi.* 1, 499–512 (1949).
14. Kennedy, B. I., Zhou, Q., Ismamnandar, Kubota, Y. & Kato, K. Cation disorder and phase transitions in the four-layer ferroelectric Aurivillius phases ABi$_2$Ti$_5$O$_{12}$ (A=Ca, Sr, Ba, Pb). *J. Solid State Chem.* 181, 1377–1386 (2008).
15. Watanabe, T. & Funakubo, H. Controlled crystal growth of layered-perovskite thin films as an approach to study their basic properties. *J. Appl. Phys.* 100, 051602–1–051602–11 (2006).
16. Irie, H. & Miyayama, M. Dielectric and ferroelectric properties of SrBi$_2$Ti$_4$O$_{12}$ single crystals. *Appl. Phys. Lett.* 79, 251–253 (2001).
17. Takahashi, K. et al. Thickness dependence of dielectric properties in bismuth layer-structured dielectrics. *Appl. Phys. Lett.* 89, 082901–1–082901–3 (2006).
18. Kojima, T. et al. Anisotropic electrical properties in bismuth layer structured dielectrics with natural super lattice structure. *Appl. Phys. Lett.* 101, 012907–1–012907–4 (2012).
19. Shibata, T., Fukuda, K., Ebina, Y., Kogure, T. & Sasaki, T. One-nanometer-thick seed layer of unilamellar nanosheets promotes oriented growth of oxide crystal films. *Adv. Mater.* 20, 231–235 (2008).
20. Ma R. & Sasaki, T. Nanosheets of Oxides and Hydroxides. Ultimate 2D charge-bearing functional crystallites. *Adv. Mater.* 22, 5082–5104 (2010).
21. Takahashi, K. et al. Thermal stability of SrRuO$_3$ bottom electrode and electric property of Pb(Zr,Ti)O$_3$ thin film deposited on SrRuO$_3$. *Ipn. J. Appl. Phys.* 41, 6873–6876 (2002).
22. Takahashi, K. et al. Effect of strain in epitaxially grown SrRuO$_3$ thin films on crystal structure and electric properties. *Ipn. J. Appl. Phys.* 41, 5376–5380 (2002).
23. Sun, C., Wang, X., Ji, A. & Li, L. Low-temperature sintering of negative-positive-zero-type temperature-stable ceramics with ZnO-B$_2$O$_3$ flux and SrCO$_3$ additive. *Ipn. J. Appl. Phys.* 50, 081501–1–081501–4 (2011).
24. Osada, M. & Sasaki, T. Two-dimensional dielectric nanosheets: novel nanoelectronics from nanocrystal building blocks. *Adv. Mater.* 24, 210–228 (2012).
25. Li, B.-W. et al. Engineered interfaces of artificial perovskite oxide superlattices via nanosheet deposition process. *ACS Nano* 4, 6673–6680 (2010).
Author Contributions
J.K. mainly contributed to this work. H.F. supervised the project. J.T. and M.M. helped to prepare film samples and analyse the data. T.S. and H.U. discussed the results and helped write the paper. T.S., M.O. and T.S. prepared the Ca$_2$Nb$_3$O$_{10}^-$ nanosheets on glass substrates and contributed to the paper. T.K., T.S. and T.K contributed to the microstructure analysis.

Additional Information
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Kimura, J. et al. Thermally stable dielectric responses in uniaxially (001)-oriented CaBi$_4$Ti$_4$O$_{15}$ nanofilms grown on a Ca$_2$Nb$_3$O$_{10}^-$ nanosheet seed layer. Sci. Rep. 6, 20713; doi: 10.1038/srep20713 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/