Mesostructured HfO$_2$/Al$_2$O$_3$ Composite Thin Films with Reduced Leakage Current for Ion- Conducting Devices

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ABSTRACT: Mesoporous hafnium dioxide (HfO$_2$) thin films (around 20 nm thick) were fabricated by a sol–gel-based spin-coating process, followed by an annealing process at 600 °C to realize the ion-conducting media for the ionics (e.g., Na$^+$ and K$^+$ for rechargeable ion batteries). Another film of aluminum metal (10 nm thick) was deposited by direct current sputtering to soak into the mesopores. A monitored thermal treatment process at 500 °C in the air yields mesostructured HfO$_2$/Al$_2$O$_3$ composite thin films. However, aluminum dioxide (Al$_2$O$_3$) is formed during annealing as an insulating film to reduce the leakage current while retaining the ionic conductivity. The obtained mesostructured HfO$_2$/Al$_2$O$_3$ films show a leakage current at 3.2 × 10$^{-9}$ A cm$^{-2}$, which is significantly smaller than that of the mesoporous HfO$_2$ film (1.37 × 10$^{-5}$ A cm$^{-2}$) or HfO$_2$/Al film (0.037 A cm$^{-2}$) at a bias voltage of 1.0 V, which is enough for ion conduction. In the meantime, among all the thin films, the mesostructured HfO$_2$/Al$_2$O$_3$ composite thin films display the smallest Nyquist arc diameter in 1.0 M KOH electrolyte, implying a lower impedance at the electrode/electrolyte interface and reflecting a better ion diffusion and movement.

INTRODUCTION

Thin films of hafnium dioxide (HfO$_2$) have received considerable attention as a dielectric material so far. 1–6 Consequently, several approaches have been proposed to improve the electrical and physical properties of HfO$_2$. Yang et al. 7 and Liu et al. 8 were the first to report on the formation of an amorphous mesoporous HfO$_2$ framework through a chemical method using block copolymers and surfactants as sacrificial templates. The mesoporosity throughout the entire morphology improved the thermal stability of HfO$_2$ as well as provided a high specific surface area for further catalytic applications. For example, H(CH$_2$CH$_2$CH$_2$)$^{89}$O(CH$_2$CH$_2$)$_{79}$OH block copolymer (abbreviated as KLE) was used as a structure-directing large agent that generated a distorted cubic arrangement of spherical mesopores in crystalline HfO$_2$ thin films. 9,10 The main benefit of the block copolymer is that it stabilizes the mesostructure of hafnium oxide up to 450 °C due to the stability of the polymer. In the same context, Malfatti and co-workers prepared HfO$_2$ films with a highly ordered rhombohedral mesostructure using a commercial Pluronic F-127 triblock copolymer. 11–13 The hafnia thin films were tunable, which gave a chance to control the reversible disorder–order transitions in the mesophase by changing the relative humidity and using X-ray. Other advantages in this context are that mesoporous materials are extensively studied for ion-conductive devices, such as rechargeable ion batteries. 8 The pores provide large channels and a short diffusion distance for facile ion mass transportation.

On the other hand, HfO$_2$-based ceramic thin films were proposed to stabilize hafnias thin films. 9,10 In this scenario, Park et al. reported the addition of aluminum dioxide (Al$_2$O$_3$) to HfO$_2$ thin films by a plasma-enhanced atomic layer deposition method. 11 The HfO$_2$ thin films are completely stabilized at room temperature and the crystallographic direction was changed to the preferred (002) orientation (i.e., tetragonal phase), resulting in an increase in the dielectric constant (47), which is approximately twice the reported value for the HfO$_2$ film with a monoclinic phase. In addition, Zheng et al. reported the direct growth of Al$_2$O$_3$-doped HfO$_2$ films onto graphene by H$_2$O-based atom layer deposition (ALD). Al$_2$O$_3$ acted as a network modifier, maintained the amorphous structure of the film even to 800 °C, and made the film smooth with a root mean square roughness of 0.8 nm. 12 Although ALD produces uniform films, it introduces undesired impurities or break the chemical bonds of graphene, resulting in a significant degradation in carrier mobility. 13–15 Meanwhile, aluminum dioxide (Al$_2$O$_3$) is an appropriate material for HfO$_2$-based ceramics because of its unique insulating properties for gate...
Mesoporous metal oxide thin films can offer a good template for engineering strains. Recently, we used mesoporous materials for vertical strain engineering in nanostructured SrTiO3 and BaTiO3 layers through an easy chemical method. The dielectric and ferroelectric properties and Curie temperature ($T_c$) are improved in the case of highly strained mesostructured SrTiO3/BaTiO3 composite thin films. This concept was further developed recently for the preparation of multilayered hybrid thin films composed of nanostructured SrTiO3 and BaTiO3 layers, which had a very low leakage current of $1.3 \times 10^{-9}$ A cm$^{-2}$ at 1.0 V compared to that of SrTiO3 or bilayer SrTiO3/BaTiO3 thin films ($0.01$ A cm$^{-2}$) in Pt/SrTiO3/BaTiO3/Pt dielectric capacitor.

In this contribution, mesoporous HfO2 thin films (around 20 nm thick) were fabricated by the sol–gel–spin-coating process followed by controlled annealing treatments at 600 °C in air to realize the ion conducting media for ionics in ion-conducting deceives. Unfortunately, a former porous medium such as a mesoporous HfO2 was so leaky that it cannot give higher bias and shows low stability. Therefore, we used the mesoporous HfO2 thin films as hard templates for scalable crystallization of highly strained Al2O3 crystals soaked inside the mesopores. To control the growth of Al2O3 inside the mesopores, we performed regulated annealing in air, which helps in the fusion of Al2O3 in the mesoporous frameworks gradually. Moreover, an insulating thin film of Al2O3 is formed on the surface of the mesoporous HfO2 film to improve the stability and reduce the leakage current while keeping the ionic conductivity. The interstitial surface area between the two materials is expected to greatly improve because of the concave shape of the mesoporous framework. This advantage gives an opportunity for crystal lattice changes to reduce the leakage current of the HfO2/Al2O3 composite layers, keep the mesoporous structure intact, and improve the stability.

### RESULTS AND DISCUSSION

For the preparation of mesoporous HfO2 thin films on Si and/or Si/SiO2/Ti/Pt substrates, Pluronic F-127 was used as a soft template. The porous textural characteristics of the thin films were controlled by tuning the amounts of Pluronic F-127 and calcination temperature (Table 1). On the other hand, for the synthesis of mesostructured HfO2/Al2O3 composite thin films, a 10 nm thick Al layer was coated on HfO2 by direct current (DC) sputtering, which when heated at 500 °C oxidizes and converts into Al2O3 fused inside the mesopores of the HfO2 framework thin film.

The optimum ratios of the block copolymer to the inorganic source ($\text{HCl}_4$) were investigated. The weight ratios of Pluronic F-127 to HfCl4 were varied from 0.6 to 1.4 (Table 1). The surface morphology of the obtained thin films calcined at 600 °C was examined using a scanning electron microscope (SEM) (Figure 1). It is observed that the films are distorted and cracked with the increase of the amount of Pluronic F-127. This was confirmed by two-dimensional (2D) grazing-incidence small-angle scattering (SAXS) images and the corresponding patterns, as shown in Figure 2. The film obtained with low amount of Pluronic F-127 showed the most intense peak at around $2\theta = 0.49^\circ$ ($d = 18.01$ nm) derived from the well-ordered close-packing of the mesopores (Figure 2a). Therefore, the preferred weight ratio of Pluronic F-127 to HfCl4 is 0.6 to form well-ordered mesoporous HfO2 frameworks. The crystal structure of the obtained mesoporous framework was examined using a wide-angle 2D X-ray powder diffraction (XRD) (Figure S1). All the mesoporous HfO2 thin films obtained at different weight ratios showed diffraction peaks consistent with a monoclinic HfO2 (PDF Card No. 00-006-0318). The structure and elemental distribution of Hf and O atoms were investigated by energy-dispersive X-ray (EDX) spectrometers attached to the SEM (Figure S2). The film is composed of Hf and O atoms homogeneously distributed over the entire mesoporous HfO2 thin films.

To study the effect of the calcination temperature on the crystallinity and morphology of the mesoporous HfO2 framework, we applied various calcination temperatures in air to remove the organic template. From the SEM images, it is obvious that calcination at 400 and 500 °C is not enough to

| sample  | pluronic F-127 (g) | H2O (g) | tetrahydrofuran (THF) (mL) | ethyl alcohol (ETOH) (g) | HfCl4 (g) | F127/HfCl4 (wt/wt) |
|---------|-------------------|---------|---------------------------|--------------------------|------------|-------------------|
| HfO2_1  | 0.30              | 0.40    | 10.0                      | 8.00                     | 0.50       | 1.40              |
| HfO2_2  | 0.40              | 0.40    | 10.0                      | 8.00                     | 0.50       | 1.20              |
| HfO2_3  | 0.50              | 0.40    | 10.0                      | 8.00                     | 0.50       | 1.00              |
| HfO2_4  | 0.60              | 0.40    | 10.0                      | 8.00                     | 0.50       | 0.80              |
| HfO2_5  | 0.70              | 0.40    | 10.0                      | 8.00                     | 0.50       | 0.60              |

**Table 1. Starting Precursors for the Formation of Several Mesoporous HfO2 Thin Films**
totally remove the template (Figure S3a,b). Meanwhile the films obtained at 400 and 500 °C are amorphous because of, may be, the incomplete removal of organic residues (Figure S4a,b). By further increase in the calcination temperature up to 700 and 800 °C, the mesoporous framework is collapsed by further crystallization (Figure S3c,d). The crystallinity of the corresponding films is improved, as shown in Figure S4c,d. Although the crystallinity is improved at elevated temperatures, collapsing the mesoporous framework destroys the mesoporous pass, which is not favorable for the movement of ions. Moreover, from 2D GI-SAXS images and the corresponding patterns (Figure S5), the films obtained at 400, 500, 700, and 800 °C did not show any ordering or periodicity of the mesopores. Therefore, the optimum calcination temperature to remove the template and obtain well-ordered mesoporous HfO2 thin films with a crystallized framework is 600 °C.

The mesoporous HfO2 thin films obtained at optimum conditions were further characterized using a transmission electron microscope (TEM), as shown in Figure 3a. The thin film shows a porous nature and, at the same time, the selected area electron diffraction image (ED; inset of Figure 3a) shows intense diffraction spots corresponding to the (102), (221), and (011) reflections of the monoclinic phase (PDF Card No. 00-006-0318).21 The crystalline nature of the mesoporous framework was further examined by a high-resolution TEM (HRTEM), as shown in Figure 3b. Well-organized and ordered atomic lattices reveal the single crystalline nature of the framework. The high-angle annular dark filed-scanning transmission electron microspore (HAADF-STEM; Figure 3c) and the corresponding elemental mapping of Hf and O atoms reflects the porous nature of the film, which is composed of Hf and O atoms with a homogeneous distribution over the entire thin film.

The optimized mesoporous HfO2 thin films were used as a template for strain engineering and scalable formation of Al2O3 crystals. Engineering strains in metal oxide thin films received a great consideration for controlling structural, electronic, and magnetic properties in many functional systems.22−30 Suzuki et al. have reported the use of mesoporous SrTiO3 thin films to engineering strains in BaTiO3 crystals through a surfactant-templated sol−gel method.17 The obtained mesostructured SrTiO3/BaTiO3 composite thin films with a large number of strains showed a dramatic enhancement of ferroelectric property. This result opened a door for strain engineering using mesoporous inorganic thin films for dielectric capacitors and enhancing strain-driven functionalities.18,31 Herein, for controlling the crystallization of Al2O3 crystals and creating strains, the mesoporous HfO2 is used as a template. The crystalline nature of HfO2/Al2O3 composite thin films was examined using a wide-angle 2D XRD (Figure 4). The peaks

Figure 2. Two-dimensional (2D) GI-SAXS patterns and the corresponding in-plane diffraction profiles of the mesoporous HfO2 films prepared using (a) 0.3 g, (b) 0.4 g, (c) 0.5 g, and (d) 0.6 g of Pluronic F-127 triblock copolymer on the surface of Si substrate at 600 °C.

Figure 3. (a) TEM (inset: SAED), (b) HRTEM, (c) HAADF-STEM, and the corresponding elemental mapping images of mesoporous HfO2 thin films prepared using 0.3 g of Pluronic F-127 triblock copolymer on the surface of Si substrate at 600 °C (the optimum mesoporous sample).

Figure 4. (a, b) Wide-angle 2D XRD images and (c) the corresponding diffraction patterns of mesostructured HfO2/Al2O3 composite thin films prepared on the Si/SiO2/Ti/Pt substrate.
positions are assignable to an orthorhombic HfO₂ phase\(^{32}\) (PDF Card No. 00-040-1173) and polycrystalline Al₂O₃\(^{33-36}\). From the elemental mapping, the thin film was further investigated by EDX spectrometers attached to the SEM (Figure 6a,b). Obviously, thin film of Al₂O₃ formed in the top with high insulating property. The HRTEM of a selected area reflects the interference of different atomic lattices coming from both HfO₂ and Al₂O₃ (Figure 5b). The structure and elemental distribution of Hf, Al, and O atoms were investigated by EDX spectrometers attached to the SEM (Figure 6a,b). Obviously, thin film of the mesostructured HfO₂/Al₂O₃ composite was obtained on the Pt substrate. From the elemental mapping, the film is composed of Hf, Al, and O atoms with heterogeneous distributions in a layered manner.

The reduction of leakage current of hafnias thin films is a crucial factor for their potential in electric applications. In capacitors, the leakage current behaviors have been extensively investigated and some leakage mechanisms have been proposed to account for the corresponding results, for example, formation of composite thin films was found to greatly affect electrical properties.\(^{37}\) In this study, we develop a synthetic approach for the formation of mesostructured HfO₂/Al₂O₃ composite thin films to monitor current passage. The schematic illustration of the fabricated electrode is presented in Figure 7a. The diameter of the upper Pt electrode was monitored to be 125 μm using a Pt mask (Figure 7b). A mesoporous HfO₂ thin film was fabricated by a spin-coating process with a speed of 3000 rpm min\(^{-1}\) for 45 s on top of the Pt substrate (Figure 7c). The film thickness was determined by cross-sectional SEM to be around 20 nm (Figure 7d). The deposition of a 10 nm thick film of Al metal by DC sputtering, the regulated thermal treatments produced Al₂O₃ inside the pores of the HfO₂ film, yielding a mesostructured HfO₂/Al₂O₃ composite thin film, as well as a thinner Al₂O₃ film at its surface (Figure 7e). The overall thickness of the mesostructured HfO₂/Al₂O₃ film was measured to be around 30 nm (Figure 7f).

We performed electrical measurements of HfO₂, HfO₂/Al, and HfO₂/Al₂O₃ thin films prepared on the Pt electrode in a vertical direction with microscale electrodes (Figure 8). The HfO₂ and HfO₂/Al thin films showed high leakage currents at around 1.37 × 10⁻⁸ and 10.5 A cm⁻² at 1.0 V, respectively, revealing the low stability of the HfO₂ and HfO₂/Al thin films and suggesting that the mesoporous framework is not able to effectively reduce the passage of current at a high bias, which is suitable for ion-conducting devices. In contrast, the mesostructured HfO₂/Al₂O₃ composite thin films show a significant low leakage current of 3.2 × 10⁻⁹ A cm⁻² at 1.0 V. We anticipate that the improvement of the leakage current in the case the mesostructured HfO₂/Al₂O₃ composite thin films is caused by the effective stress caused at the interfaces between the HfO₂ and Al₂O₃ domains. This phenomenon is being revealed by the new research on strain engineering/lattice changes and their effects on the electric properties. For example, so far, Choi et al. demonstrated the improvement of ferroelectricity in strained BaTiO₃ thin films.\(^{38}\) At the same time, during the formation of Al₂O₃ crystals, a phase transformation of the monoclinic HfO₂ to the (012)
orientation (orthorhombic phase) occurred. The improved crystallinity resulted in the increasing stability of HfO2 thin films, resulting in a remarkable enhancement of reduced leakage current. Additionally, formation of a highly resistive thin film of Al2O3 on the surface of mesoporous HfO2 reduces the electric current because of its high insulating property.

For faster ion movements, a higher bias is needed. However, a former porous medium such as a mesoporous HfO2 film was so leaky that it cannot give a higher bias and shows low stability. Therefore, we designed the new mesostructured HfO2/Al2O3 composite thin films for easy ion movement with a lower electron current (higher insulating property). The deposited Al2O3 covers the surface of the porous nanohole to reduce the surface states, which contributes to the leak current while keeping the porous structure intact. To check the conductivity of our sample thin films, we performed electrochemical impedance spectroscopy (EIS) in 1.0 M KOH at 0.7 V in the frequency range from 0.01 Hz to 100 kHz. The Nyquist complex-plane impedance spectra of the thin films are shown in Figure 9. Among all the thin films, the mesostructured HfO2/Al2O3 composite thin films display the smallest arc diameter, implying a lower impedance at the electrode/electrolyte interface and reflecting better ion diffusion and movement at the electrode/electrolyte interface.

**CONCLUSIONS**

Formation of a highly ordered mesoporous HfO2 thin film prepared by the sol–gel method to control the growth of Al2O3 inside the porous framework is reported. In the first stage, the mesoporous thin film of HfO2 is prepared by sol–gel-based spin-coating processes. Pluronic F-127 triblock copolymer is used as a template and subsequent annealing in air is applied in the final stage to remove it. Another film of aluminum metal (10 nm thick) was developed by DC sputtering in the second stage. A controlled thermal treatment in aerobic of HfO2/Al layers results in the oxidation of aluminum metal and its fusion inside and on the top of the mesopores HfO2 thin films. The mesostructured HfO2/Al2O3 composite thin films with a much reduced leakage current compared to that of HfO2 or HfO2/Al thin films were obtained. Our synthetic approach is easy and economical.

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**Figure 7.** (a) Schematic illustration of the fabricated electrode. SEM images of (b) the top Pt electrode, (c) mesoporous HfO2, and (e) mesostructured HfO2/Al2O3 composite thin films prepared on the Si/SiO2/Ti/Pt substrate. Cross-sectional SEM images of (d) mesoporous HfO2, and (f) mesostructured HfO2/Al2O3 composite thin films prepared on the Si/SiO2/Ti/Pt substrate.

**Figure 8.** J−V curves to determine the leakage current of mesoporous HfO2 thin films obtained at 600 °C, HfO2/Al double layers, and mesostructured HfO2/Al2O3 composite thin films prepared on Si/SiO2/Ti/Pt substrate.

**Figure 9.** Electrochemical impedance spectra (EIS) of mesoporous HfO2 thin films obtained at 600 °C, HfO2/Al double layers and mesostructured HfO2/Al2O3 composite thin films prepared on the Si/SiO2/Ti/Pt substrate.
compared to the complicated and expensive physical deposition technology, and we anticipate that our concept will open the door for the fabrication of ion conducting devices in the future.

■ EXPERIMENTAL DETAILS

**Chemicals.** Pluronic F-127 and hafnium(IV) chloride (99.9%) were purchased from Sigma-Aldrich, Co. Ethanol (99.5%), tetrahydrofuran (98%), and potassium hydroxide solution (1 M KOH) were purchased from Nacalai Tesque, Inc. All chemicals were used as delivered with no further purifications.

**Fabrication of Substrates.** The substrates were prepared in typical procedures of our previously published article using p-type Si(100) wafers of 1–10 Ω cm with a thermal SiO2 film (200 nm thick) purchased from AKI Corporation. OFPR-800LB photoresist purchased from Tokyo Ohka was spin-coated on the wafer surface for protection. By applying O2 plasma for 3 min with O2 flow of 100 sccm, radio frequency and power of 300 W for cleaning, the wafer was heated on a hotplate at 120 °C for more than 1 min. Hexamethyldisilazane (HMDS “OAP”) purchased from Tokyo Ohka was spin-coated as an adhesion promoter with a spin rate of 3000 rpm for 5.0 s. For a second round to protect the surface, OFPR-800LB photoresist was spin-coated, and the wafer was subsequently heated on a hotplate for drying the resist film at 120 °C for 5 min. The substrate was fixed on an adhesive sheet with the backside up for dicing and the following parameters were used: blade width: 30 μm, wafer thickness: 380 μm, blade thickness: 130 μm, wafer thickness: 1.0 cm2, and cutting speed: 1000 μm/s.

**Preparation of Mesoporous HfO2 Thin Films.** Different amounts of Pluronic F-127 were used (Table 1). In a typical procedure, Pluronic F-127 was dissolved in 10 mL of THF under stirring at room temperature until the solution became transparent (A). Another solution is prepared by dissolving 0.5 g of HMDS in H2O (0.4 g) and ETOH (8.0 g) under stirring until a clear solution (B) was obtained. The two solutions are mixed dropwise, and the stirring is continued for 5 h to get the sol. The film is prepared into the substrate by spin-coating at a rotation rate of 300 rpm s−1 for 40 s. After coating, the film is transferred to a humidity chamber (95 %) and aged for 10 min−1 to improve the metal framework cross-linking. The template is removed by heating at the designated temperature (400, 500, 600, 700, and 800 °C) for 1 h with a heating rate of 5 °C min−1. All calcination processes are carried out in the aerobics.

**Preparation of Mesostructured HfO2/Al2O3 Composite Thin Films.** An Al metal layer (10 nm thick) was coated on HfO2 by DC sputtering at a very low pressure. By heating at 500 °C, the Al metal oxides and converts into Al2O3 fused inside and on the top of the mesopores of HfO2 framework to form the mesostructured HfO2/Al2O3 composite thin films. The upper Pt electrode (150 nm thick) was fabricated by DC sputtering using a shadow metal mask with a diameter of 120 μm.

**Characterization.** Electron microscopy images were collected using a Hitachi SU8000 scanning electron microscope at an accelerating voltage of 5 kV and current of 10 mA. A JEM-2100F TEM system operated at 200 kV and attached to an energy-dispersive X-ray (EDX) spectroscope was used for elemental mapping. X-ray diffraction (XRD) measurements were performed by a Rigaku RINT 2500X diffractometer with a monochromated Cu Kα radiation (40 kV, 40 mA) at a low scan rate (0.5 °C min−1). Two-dimensional X-ray diffraction (2D XRD) analyses were carried out using a Bruker D8 XRD system. Small-angle X-ray scattering (SAXS) analyses (GI mode) and the corresponding low-angle XRD profiles were obtained using a Nano Viewer (Rigaku, Japan) SAXS instrument attached to a Micro Max-007 HF high-intensity microfocus rotator anode X-ray generator within 8 h at λ = 0.1540 nm of the X-ray beam. The d-spacing of the mesopores was calculated using Bragg’s law (2d sin θ = nλ). Current density—voltage (J–V) measurements were performed using a source-measurement unit (Keithley, 2612B) and LCR meter (Agilent E4980A), respectively, at a current compliance of 1 mA. The electrochemical impedance spectroscopy (EIS) was performed on a CHI 660EZ electrochemical workstation using a conventional three-electrode cell. Carbon rod was used as a counter electrode and a saturated calomel electrode served as a reference electrode. The mesoporous HfO2 thin films obtained at 600 °C, HfO2/Al2O3 double layers, and mesostructured HfO2/Al2O3 composite thin films prepared on Si/SiO2/Ti/Pt substrate (1.0 cm2) were used as working electrodes.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01095.

Wide-angle 2D XRD patterns of the mesoporous HfO2 films prepared using (a) 0.3 g, (b) 0.4 g, (c) 0.5 g, and (d) 0.6 g of Pluronic F-127 triblock copolymer on the surface of Si substrate at 600 °C; energy-dispersive X-ray spectroscopy (EDX) results of the mesoporous HfO2 films prepared using 0.3 g of Pluronic F-127 triblock copolymer on the surface of Si substrate at 600 °C: (a) SEM image, (b) EDX spectrum, and elemental mapping of (c) Hf, (d) O, and (e) Si (Si is the substrate); SEM images of the mesoporous HfO2 thin films obtained at various temperatures (i.e. (a) 400 °C, (b) 500 °C, (c) 700 °C, and (d) 800 °C) using Pluronic F-127 triblock copolymer on the surface of Si substrate; wide-angle 2D XRD patterns of the mesoporous HfO2 thin films obtained at various temperatures (i.e. (a) 400 °C, (b) 500 °C, (c) 700 °C, and (d) 800 °C) using Pluronic F-127 triblock copolymer on the surface of Si substrate; 2D GI-SAXS patterns and the corresponding in-plane diffraction profiles of the mesoporous HfO2 films at various temperatures (i.e. (a) 400 °C, (b) 500 °C, (c) 700 °C, and (d) 800 °C) using Pluronic F-127 triblock copolymer on the surface of Si substrate; EDX results of the HfO2/Al2O3 composite thin films prepared on Si/SiO2/Ti/Pt substrate: (a) SEM image, and (b) EDX
spectrum, and elemental mapping of (c) Hf, (d) Al, (e) O, and (f) Pt (Pt is the substrate) (PDF)

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**Notes**
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REFERENCES

(1) Ting, G. G.; Acton, O.; Ma, H.; Ka, J. W.; Jen, A. K. Study on the Formation of Self-Assembled Monolayers on Sol-Gel Processed Hafnium Oxide as Dielectric Layers. *Langmuir* 2009, 25, 2140.

(2) Jiang, K.; Anderson, J. T.; Hoshino, K.; Li, D.; Wager, J. F.; Keszler, D. A. Low-Energy Path to Dense HfO2 Thin Films with Aqueous Precursor. *Chem. Mater.* 2011, 23, 945.

(3) Everaerts, K.; Emery, J. D.; Jariwala, D.; Karmel, H. J.; Sangwan, V. K.; Prabhunirmashi, P. L.; Geier, M. L.; McMorrow, J. J.; Bedzyk, M. J.; Facchetti, A.; Hersam, M. C.; Marks, T. J. Ambient-Processable Transition-Metal Oxides. *J. Am. Chem. Soc.* 2013, 135, 8926.

(4) Yang, P.; Zhao, D.; Margoless, D. I.; Chmelka, B. F.; Stucky, G. D. Block Copolymer Templating Syntheses of Mesoporous Metal Oxides with Large Ordering Lengths and Semicrystalline Framework. *Chem. Mater.* 1999, 11, 2813.

(5) Liu, P.; Liu, J.; Sayari, A. Preparation of Porous Hafnium Oxide in The Presence of a Catonic Surfactant. *Chem. Commun.* 1997, 577.

(6) Brezesinski, T.; Smarsly, B.; Iimura, K.; Grosso, D.; Boissiere, C.; Amenitsch, H.; Antonietti, M.; Sanchez, C. Self-assembly and Crystallization Behavior of Mesoporous, Crystalline HfO2 Thin Films: a Model System for The generation of Mesostructured Transition-Metal Oxides. *Small* 2005, 1, 889.

(7) Malfatti, L.; Kichchob, T.; Costacurta, S.; Falcado, P.; Schiavuta, P.; Amenitsch, H.; Innocenzi, P. Highly Ordered Self-Assembled Mesostructured Hafnia Thin Films: An Example of Rewritable Mesostructure. *Chem. Mater.* 2006, 18, 4553.

(8) Santhoshkumar, P.; Prasanna, K.; Jo, Y. N.; Sivagami, I. N.; Kang, S. H.; Lee, C. W. Hierarchically Structured Mesoporous Bimetallic Oxides as a Potential Anode Material for Rechargeable Lithium Batteries. *J. Alloys Compd.* 2019, 771, 555.

(9) Shimizu, T.; Katayama, K.; Kiguchi, T.; Akama, A.; Konno, T. J.; Sakata, O.; Funakubo, K. The Demonstration of Significant Ferroelectricity in Epitaxial Y-Doped HfO2 Film. *Sci. Rep.* 2016, 6, No. 2931.

(10) Nie, X.; Ma, D.; Ma, F.; Xu, K. Thermal Stability, Structural and Electrical Characteristics of The modulated HfO2/Al2O3 Films Fabricated by Atomic Layer Deposition. *J. Mater. Sci.* 2017, 52, 11524.

(11) Park, P. K.; Kang, S.-W. Enhancement of Dielectric Constant in HfO2 Thin Films by The addition of Al2O3. *Appl. Phys. Lett.* 2006, 89, 192905.

(12) Zheng, L.; Cheng, X.; Yu, Y.; Xie, Y.; Li, X.; Wang, Z. Controlled Direct Growth of Al2O3-doped HfO2 Films on Graphene by H2O-based Atomic Layer Deposition. *Phys. Chem. Chem. Phys.* 2015, 17, 3179.

(13) Zheng, L.; Cheng, X.; Cao, D.; Zhang, D.; Wang, Z.; Xu, D.; Xia, C.; Shen, L.; Yu, Y. Al2O3-Gd2O3 dual-films grown on graphene directly by H2O-assisted atomic layer deposition. *RSC Adv.* 2014, 4, 44296.

(14) Zheng, L.; Cheng, X.; Cao, D.; Wang, G.; Wang, Z.; Xu, D.; Xia, C.; Shen, L.; Yu, Y.; Shen, D. Improvement of Al2O3 Films on Graphene Grown by Atomic Layer Deposition with Pre-H2O Treatment. *ACS Appl. Mater. Interfaces* 2014, 6, 7014.

(15) Zheng, L.; Cheng, X.; Cao, D.; Wang, Z.; Xia, C.; Yu, Y.; Shen, D. Property Transformation of Graphene with Al2O3 Films Deposited Directly by Atomic Layer Deposition. *Appl. Phys. Lett.* 2014, 104, 023112.

(16) Lin, H. C.; Ye, P. D.; Wilk, G. D. Leakage Current and Breakdown Electric-Field Studies on Ultrathin Atomic-Layer-Deposited Al2O3 on GaAs. *Appl. Phys. Lett.* 2005, 87, 182904.

(17) Suzuki, N.; Zakaria, M. B.; Torad, N. L.; Wu, K. C.; Nemoto, Y.; Imura, M.; Osada, M.; Yamauchi, Y. Synthesis of Highly Strained Mesostructured SrTiO3/BaTiO3 Composite Films with Robust Ferroelectricity. *Chem. - Eur. J.* 2013, 19, 4446.

(18) Zakaria, M. B.; Nagata, T.; Matsuda, A.; Yasuhara, Y.; Ogura, A.; Hossain, M. S. A.; Billah, M.; Yamauchi, Y.; Chikyow, T. Chemical Synthesis of Multilayered Mesostructured Nanostructured Thin Films with Dielectric Features for Ultra Capacitors. *ACS Appl. Nano Mater.* 2018, 1, 915.

(19) Audoit, G.; Mhuircheartaigh, E. N.; Lipson, S. M.; Morris, M. A.; Blau, W. J.; Holmes, J. D. Strain Induced Photoluminescence from Silicon and Germanium Nanowire Arrays. *J. Mater. Chem.* 2008, 18, 4809.

(20) Cao, J.; Ertekin, E.; Srinivasan, V.; Fan, W.; Huang, S.; Zheng, H.; Yim, J. W.; Khanal, D. R.; Ogletree, D. F.; Grossman, J. C.; Wu, J. Strain Engineering and One-Dimensional Organization of Metal-Insulator Domains in Single-crystal Vanadium Dioxide Films. *Nat. Nanotechnol.* 2009, 4, 732.

(21) Gallana, B.; Benedicto, M.; Vazquez, L.; Molina-Aldareguia, J. M.; Tejedor, P. Thermal Stability of HfO2-on-GaAs Nanopatterns. *Nanoscale* 2012, 4, 3734.

(22) Breckenfeld, E.; Kim, H.; Burgess, K.; Charipar, N.; Cheng, S. F.; Stroud, R.; Pique, A. Strain Effects in Epitaxial VO2 Thin Films on Columnar Buffer-Layer TiO2/Al2O3 Virtual Substrates. *ACS Appl. Mater. Interfaces* 2017, 9, 1577.

(23) Guzmán, R.; Maurel, L.; Langenberg, E.; Lupini, A. R.; Algarabel, P. A.; Pardo, J. A.; Magen, C. Polar-Graded Multiferroic SrMnO3 Thin Films. *Nano Lett.* 2016, 16, 2221.

(24) Chandrasena, R. U.; Yang, W.; Lei, Q.; Delgado-Jaime, M. U.; Wijseseka, K. D.; Golalikhani, M.; Davidson, B. A.; Arenholza, E.; Kobayashia, K.; Kobatab, M.; de Groota, F. M.; Aschaiera, U.; Spaldina, N. A.; Xi, X.; Gray, A. X. Strain-Engineered Oxygen Vacancies in CaMnO3 Thin Films. *Nano Lett.* 2017, 17, 794.

(25) Agar, J. C.; Damodaran, A. R.; Velarde, G. A.; Pandya, S.; Mangalam, R. V.; Martin, L. W. Complex Evolution of Built-in Potential in Compositionally-Graded Pb5Sr1-xTiO3 Thin Films. *ACS Nano* 2015, 9, 7332.

(26) Feng, Q.; Zhao, S.; He, D.; Tian, S.; Gu, L.; Wen, X.; Chen, C.; Peng, Q.; Wang, D. Li. Y. Strain Engineering to Enhance the Electrooxidation Performance of Atomic-Layer Pt on Intermetallic Pt,Ga. *J. Am. Chem. Soc.* 2018, 140, 2773.

(27) Mazumdar, D.; Shelke, V.; Iliev, M.; Jesse, S.; Kumar, A.; Kalinin, S. V.; Baddorf, A. P.; Gupta, A. Nanoscale Switching Characteristics of Nearly Tetragonal BiFeO3 Thin Films. *Nano Lett.* 2010, 10, 2555.

(28) Wölz, M.; Ramsteiner, M.; Kaganer, V. M.; Brandt, O.; Geelhaar, L.; Rieuch, H. Strain Engineering of Nanowire Multi-Quantum Well Demonstrated by Raman Spectroscopy. *Nano Lett.* 2013, 13, 4053.

(29) Paskiewicz, D. M.; Scott, S. A.; Savage, D. E.; Celler, G. K.; Lagally, M. G. Symmetry in Strain Engineering of Nanomembranes: Making New Strained Materials. *ACS Nano* 2011, 5, S532.
(30) Zhao, J.; Guo, H.; He, X.; Zhang, Q.; Gu, L.; Li, X.; Jin, K. J.; Yang, T.; Ge, C.; Luo, Y.; He, M.; Long, Y.; Wang, J. O.; Qian, H.; Wang, C.; Lu, H.; Yang, G.; Ibrahim, K. Manipulating the Structural and Electronic Properties of Epitaxial SrCoO2.5 Thin Films by Tuning the Epitaxial Strain. ACS Appl. Mater. Interfaces 2018, 10, 10211.

(31) Suzuki, N.; Osada, M.; Billah, M.; Bando, Y.; Yamauchi, Y.; Hossain, S. A. Chemical Synthesis of Porous Barium Titanate Thin Film and Thermal Stabilization of Ferroelectric Phase by Porosity-Induced Strain. J. Visualized Exp. 2018, 133, e57441.

(32) Schroeder, U.; Richter, C.; Park, M. H.; Schenk, T.; Pesic, M.; Hoffmann, M.; Fengler, F. P. G.; Pohl, D.; Rellinghaus, B.; Zhou, C.; Chung, C. C.; Jones, J. L.; Mikolajick, T. Lanthanum-Doped Hafnium Oxide: A Robust Ferroelectric Material. Inorg. Chem. 2018, 57, 2752.

(33) Silva, A. S.; de Souza, S. M.; Sanches, E. A. Polypyrrole@α-Al2O3 and Polypyrrole@CeO2 Core-Shell Hybrid Nanocomposites. J. Compos. Mater. 2018, 52, 1433.

(34) Agarwal, M.; Garg, S. K.; Asokan, K.; Kumar, P. Temperature-Dependent OSL Properties of Nano-Phosphors LiAlO2:C and α-Al2O3:C Appl. Surf. Sci. 2018, 444, 819.

(35) Li, Y.; Yan, S.; Qian, L.; Yang, W.; Xie, Z.; Chen, Q.; Yue, B.; He, H. Effect of Tin on Nb2O5/α-Al2O3 Catalyst for Ethylene Oxide Hydration. J. Catal. 2006, 241, 173.

(36) Li, Z.; Wu, K.; Cao, J.; Wang, Y. Controlled Synthesis of α-Al2O3 via The Hydrothermal-Pyrolysis Method, IOP Conference Series: Materials Science and Engineering; IOP Publishing Ltd, 2017, 207, 012004.

(37) Yang, H.; Jain, M.; Suvorova, N. A.; Zhou, H.; Luo, H. M.; Feldmann, D. M.; Dowden, P. C.; DePaula, R. F.; Foltyn, S. R.; Jia, Q. X. Temperature-Dependent Leakage Mechanisms of Pt/BiFeO3/SrRuO3 Thin Film Capacitors. Appl. Phys. Lett. 2007, 91, 072911.

(38) Choi, K. J.; Biegalski, M.; Li, Y. L.; Sharan, A.; Schubert, J.; Uecker, R.; Reiche, P.; Chen, Y. B.; Pan, X. Q.; Gopalan, V.; Chen, L. Q.; Schom, D. G.; Eom, C. B. Enhancement of Ferroelectricity in Strained BaTiO3 Thin Films. Science 2004, 306, 1005.