Supporting Information

van der Waals Epitaxy of Highly (111)-Oriented BaTiO₃ on MXene

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Methods

MXene preparation

The Ti₃AlC₂ MAX phase was synthesized as described elsewhere.¹ To obtain large MXene flakes, chemical exfoliation of Ti₃AlC₂ was accomplished using a mixture of HCl-H₂O-HF solution (6:3:1). One gram of Ti₃AlC₂ powder (particle size < 38 μ m) and 40 mL of etchant solution was stirred at 500 RPM for 24 h at room temperature. Delamination of Ti₃C₂T_x was completed by the slow addition of 4 g of LiCl, to avoid overheating, and subsequent mixing. ~150 mL of deionized (DI) water was added, centrifuged at 3500 RPM for 2 min, and the supernatant was decanted. This process was repeated until a dark supernatant formed. The dark supernatant was centrifuged for 10 min to remove the remaining unetched MAX phase and the Ti₃C₂T_x. After separating the unetched MAX in the sediment, the solution was centrifuged at 3500 RPM for 1 h, and 30 mL of deionized (DI) water was added to the sediment centrifuged for five minutes. The supernatant of the delaminated Ti₃C₂T_x with a concentration around 0.5 mg/mL was used in subsequent spray-coating. To prepare delaminated-Ti₃C₂T_x solution with small MXene flakes, Ti₃AlC₂ MAX phase was etched in a mixture of LiF and HCl etchant.² Briefly, 2 g of Ti₃AlC₂ powder was added to a pre-mixed solution of 2 g of LiF and 20 mL of 9 M HCl. The reaction mixture was stirred at 35 °C for 24 h. Then the reaction mixture was washed with 9 M HCl for 3 cycles, followed by DI water for 3 cycles. The Ti₃C₂T_x solution was filtered on a polypropylene membrane (3501 Coated PP, Celgard, USA). 200 mg of finely ground powder was dispersed in 20 mL of DI water. The suspension was sonicated by a probe sonicator (FB-505, Fisher Scientific, USA) operating at 25 kHz for 30 min. The suspension was centrifuged at 3500 RPM for 1 h to collect the delaminated-Ti₃C₂T_x solution in the supernatant.

A 5 x 5 mm quartz substrate was treated with H_2SO_4 : H_2O_2 (3:1) solution (Piranha solution) for 1 h under sonication to yield a hydrophilic surface. The treated substrate was sonicated in DI water follow by acetone for 15 and 10 min, respectively. The d-Ti₃C₂T_x solution was sprayed onto the substrate by airbrush (Master Airbrush Model G-233, USA) with a 0.2 mm nozzle size and 80 psi operating pressure. After deposition of each layer, the sample was dried with an air gun (Master heater gun Model HG-201A, USA). A dip-coater (PTL-MM01, MTI Corporation, USA) was used for dip-coating. A pre-cleaned substrate was dipped in the d-Ti₃C₂T_x solution for 10 min and pulled up with a constant speed of 200 mm/min. The coated film was allowed to dry in air for about 10 min. The film was further heated at 150 °C in a vacuum oven for 3 h to remove interacted water molecules between the Ti₃C₂T_x layers.



Fig. S1 Pt substrates coated by $Ti_3C_2T_x$ by dip-coating technique. The scale bar is 5 mm.



Fig. S2 Quartz substrates spray-coated by $Ti_3C_2T_x$ with different thickness. The scale bar is 5 mm.

BaTiO₃ thin film deposition

A series of BTO films were deposited onto quartz/Ti₃C₂T_x or Si/SiO₂/Ti/Pt/Ti₃C₂T_x substrates by means of pulsed-laser deposition. The thin film depositions were conducted using commercially available polycrystalline stoichiometric ceramic targets (BaTiO₃ (BTO): Kurt J. Lesker) with a KrF excimer laser (Lamdba-Physik COMPLEX 102, λ = 248 nm) at a base chamber vacuum pressure of less than 2.0 x 10⁻⁶ Torr. Growths of the BTO films were carried out using a laser fluence of 1.30 J/cm2, at a 3 Hz repetition rate and a temperature of 700 °C and an oxygen pressure of 20 mTorr. The films were post-growth annealed in the growth chamber

(to minimize oxygen vacancy formation) for 10 min at the deposition temperature under 500 Torr of oxygen, cooled to 200 °C at 10°C/min and then finally to room temperature at a slower rate of 5 °C/min.

Al_2O_3 thin film deposition

Atomic layer deposition of the AI_2O_3 layers was conducted in a Picosun R200 Advanced reactor using trimethyl-aluminum (Alfa Aesar) and H_2O as reactants at a deposition temperature of 290 °C.

SrRuO₃ thin film deposition

The SrRuO₃ (SRO) layer was deposited by pulsed laser deposition (PLD) prior to the BaTiO₃ layer for the films in Fig. 3. The X-ray diffraction (XRD) scan below of the film in Fig. 3a reveals that the SRO layer is oriented along the (111) direction as well as the BTO layer. The 2 θ peak position of approximately 39.94° is very close the bulk pseudocubic value.³ Comparing the BTO film on the MXene spray coated quartz substrate in Fig. 2d, the SRO layer might enhance the preferred orientation along the (111) direction as the (001) and (110) peaks were not detected on the sample which had the SRO layer deposited first.



Fig. S3 XRD of SRO and BTO film grown on quartz with spray-coating MXene. The SRO and BTO films were deposited by PLD without breaking vacuum. The # denotes a peak from the sample stage.

Characterization of structure and composition

Film orientation and thickness were confirmed by X-ray diffraction and X-ray reflectivity (Rigaku SmartLab) respectively using a Cu Kα source. In-plane and out-of-plane scans were performed to determine the orientation of the BTO films and the presence of the MXene before and after the thin film deposition. The pole figure was collected using the in-plane method⁴ on the same diffractometer. Topographic height atomic force microscopy was used to determine the quality of the MXene and the deposited film surface.

The cross-section of the Pt/MXene/BTO/ Al₂O₃/Pt structure for TEM was prepared using a FEI Strata Dual Beam Focused Ion Beam - Scanning Electron Microscope equipped with an Omniprobe micromanipulator. A standard lift-out procedure was used. Transmission electron microscopy and scanning-transmission electron microscopy- energy dispersive spectroscopy experiments were performed on a JEOL JEM2100 operated at 200 keV.

Scanning Probe Microscopy (SPM)

SPM images were recorded by using a driving frequency of 304 kHz, driving amplitude 73.85 mV, and scanning frequency between 0.4 - 0.7 Hz. The thickness of the thin MXene coating on quartz substrate was 12.2 \pm 1.5 nm, while that of the thick coating was 64.0 \pm 6.9 nm as shown in Fig. S4 (a) and S5 (a), respectively. The height profiles of the thin and thick samples are shown in Fig. S4 (b) and S5 (b), respectively. Shown in Fig. S6 is an enlarged area of the thin MXene coating on quartz substrate, revealing random orientations of 2D MXene sheets of \approx 1-5 µm lateral size.



Fig. S4 (a) An SPM image of thin MXene coating on quartz and (b) Height profile of the line shown in (a).



Fig. S5 (a) An SPM image of thin MXene coating on quartz and (b) Height profile of the line shown in (a).



Fig. S6 An enlarged area SPM image of thin MXene coating on quartz.

Electrical properties measurement

Dual AC resonance tracking piezoresponse force microscopy (Asylum MFP-3D) was used to scan the Si/SiO₂/Ti/Pt/Ti₃C₂T_x BTO film over a 5 μ m x 5 μ m area with a scan speed of 1 Hz. A 6 V DC and a 4 V AC voltage was applied to the tip for the scans. The tip (Ti/Pt coated silicon with a 28 \pm 10 nm radius, Oxford Instruments-Model number AC240TM-R3) had a central frequency of 330 kHz and a quality factor of 153.4 in contact resonance. Switching spectroscopy piezoresponse force microscopy was conducted using the same conditions as above. PFM maps were also collected to verify the capability of the BTO film to be



Fig. S7 PFM image of selectively poled area showing (a) height, (b) amplitude, and (c) phase. The black dashed outline in (c) shows the pole regions.

poled.

Electrical properties measurement

Platinum top electrodes of thickness 120 nm were deposited onto the BTO films using DC magnetron sputtering with photolithographically defined electrodes of nominally 90 μ m x 90 μ m. Current vs voltage, capacitance vs voltage, and capacitance vs frequency measurements were collected on film samples placed in a probe station (Lakeshore Cryotronics TTP4) using an electrometer (Keithley SCS-4200) using a metal-insulator-metal configuration. To determine the dielectric constant of only the BTO layer in the films with BTO/ Al₂O₃ bilayer, two parallel plate capacitors in series were assumed and the dielectric constant was extracted from the total measured capacitance, using a dielectric constant of 10 for Al₂O₃ and the corresponding layer thicknesses of 3 and 100 nm for Al₂O₃ and BTO, respectively.

Lattice parameter calculations

In regards to the BTO film on MXene spray-coated quartz, the positions of (110), (211), and (220) peak from the grazing incidence scan were extracted from the scan shown in Fig. 2b. Using Bragg's Law, the interatomic spacing of the planes corresponding to each of the peaks was calculated. Using the (110) and (220) peaks, the in-plane lattice parameter *a* was calculated using the corresponding Miller indices and a tetragonal crystal structure. Since the value of *l* is zero, the calculation of the in-plane lattice parameter is straightforward. The corresponding values were averaged together to get the *a* lattice parameter value of 4.03 ±. 0.01. Using the (211) peak position and a tetragonal crystal structure, the *c* lattice parameter is calculated using the previously determined value of the *a* lattice parameter, resulting in a value of 4.04 ± 0.01 . The corresponding *c/a* ratio is $1.004 \pm .001$ showing the BTO film is in a cubic crystal structure.

The BTO film both on bare Pt-silicon and the MXene spray-coated Pt-silicon was measured using out-of-plane XRD which is shown in Fig. 2e. The (001) and (002) peaks from the Pt-silicon/BTO and the (111) peak from the Pt-Silicon/MXene/BTO were extracted. The lack of peak splitting in these scans, which would indicate a tetragonal structure, and along with the calculations from the grazing incidence scans, allows for the assumption of a cubic crystal structure for BTO thin film. Thus the out-of-plane lattice parameter is equivalent to the in-plane lattice parameter. The positions of the (001) and (002) peaks from the BTO film on bare Pt-silicon and the position of the (111) peaks on the MXene spray-coated Pt-silicon were extracted, and the interatomic spacing was calculated in the same manner as above. Using the cubic crystal structure yields an *a* lattice parameter of 4.04 ± 0.01 .

References

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