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等离子辅助制备单元层厚度的铁电薄层及其铁电性的表征

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摘要:我们报道了一种通过机械剥离和 Ar^+等离子体减薄过程的组合来制备 3.6 nm 厚的二维双(苄基铵)四氯化铅(BA_2PbCl_4)的薄层。压电力显微镜测量表明,Ar^+等离子体蚀刻后单元层厚度的 BA_2PbCl_4 薄层的铁电性仍然保持。

关键词:BA_2PbCl_4 薄层;铁电性;氩等离子体刻蚀
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Plasma-Assisted Fabrication of Ferroelectric Flakes with Single-Unit-Cell Thickness and Characterization of Ferroelectricity

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Abstract: Here, we report a successful method to fabricate a 2D bis(benzylammonium) lead tetrachloride (BA_2PbCl_4) flake with a thickness of 3.6 nm by a combination of mechanical exfoliation and an Ar^+ plasma thinning process. Piezoresponse force microscopy (PFM) measurements reveal that the ferroelectricity of the BA_2PbCl_4 flakes with single-unit-cell thickness persists after Ar^+ plasma etching.

Keywords: BA_2PbCl_4 flakes; ferroelectricity; Ar^+ Plasma etching

0 Introduction

Ferroelectrics were an important discovery in the field of modern condensate physics and are now widely used in contemporary electronic products, such as non-volatile memories, sensors and nanoscale electronic products[1-16]. In conventional ferroelectric materials (such as $BaTiO_3$), ferroelectricity originates from a permanent dipole moment that is generated by the displacement of positive and negative charge centers, resulting in spontaneous polarization, and the polarization direction can be reversed or reoriented by applying an external electric field. However, due to the discontinuity of the crystal structure in traditional three-dimensional ferroelectrics and the complicated physical and chemical environment at the interface, the polarized charge cannot be completely screened[17-22]. As a result, ferroelectrics are believed to have a critical thickness, below which the ferroelectricity vanishes due to the depolarization field.

The critical thickness is a contradiction for semiconductor miniaturization. In recent years, groups have made a breakthrough in the critical thickness of ferroelectrics[23-27], and related research has become a research hotspot in the field. At the same time, two-dimensional (2D) materials have become a good platform for the study of ferroelectricity at the critical thickness because of the high environmental stability

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and weak bonding force between adjacent layers, which has aroused widespread interest from scientific researchers[28-35]. A few years ago, Liao et al. first reported a layered perovskite material bis (benzylammonium) lead tetrachloride (BA_2PbCl_4)[36]. Because of its special perovskite structure and hybrid components, this material can perform bandgap regulation and is expected to be used in photovoltaics. Thus, You et al. fabricated BA_2PbCl_4 flakes with the thickness of one crystal layer, and the ferroelectricity of the BA_2PbCl_4 flakes with single-unit-cell thickness has been well demonstrated by the piezoresponse force microscopy (PFM) method[37]. The ferroelectric polarization direction of BA_2PbCl_4 flakes with a nanometerscale thickness is confined to within the in-plane direction. Unlike out-of-plane polarization, the in-plane polarization configuration is not easily affected by the depolarization field, so it is expected to break through the critical thickness. Hence, obtaining high-quality, large-area BA_2PbCl_4 flakes in the nanometer thickness range has become an urgent issue.

In our work, we present the first successful experimental approach to fabricate large-area and uniform BA_2PbCl_4 flakes with single-unit-cell thickness by a combination of mechanical exfoliation and subsequent Ar^+ plasma etching. The thickness change is determined by atomic force microscopy (AFM). PFM is used to characterize BA_2PbCl_4 flakes before and after Ar^+ plasma etching. Finally, the ferroelectricity of the BA_2PbCl_4 flake with single-unit-cell thickness after Ar^+ plasma treatment was demonstrated. This method enables the fabrication of large-area and uniform 2D ferroelectric flakes at nanoscale thicknesses, which facilitates the research on the critical thickness of ferroelectrics.

1 Experimental

1.1 Sample preparation

As previously reported, stoichiometric amounts of benzylammonium chloride and lead chloride were dissolved in a 95% (*n*/*n*) concentrated HCl aqueous solution at 60 ℃. Lamellar crystals of BA_2PbCl_4 were then obtained by slowly cooling the solution at a speed of 0.125 ℃·h^{-1} in an oil bath pot. These crystals were thus exfoliated onto 300 nm SiO_2/Si substrates. The BA_2PbCl_4 flakes were fabricated by the mechanical exfoliation method. Compared with the steps in the traditional mechanical cleavage method, the mechanical exfoliation method has an additional step of annealing on a conventional laboratory heat plate at 100 ℃ for 2 min (Supporting information, Fig. S1). The thickness and morphology of selected BA_2PbCl_4 flakes fabricated by the mechanical exfoliation method were determined by optical microscopy and AFM, respectively.

1.2 Plasma treatment

The plasma (commercial 0.5 MHz inductively coupled plasma (ICP) source) was used to etch the thickness of the BA_2PbCl_4 flakes without any external heating. To ensure that the BA_2PbCl_4 flakes can be etched evenly, the sample stage was kept rotated at an even speed during the entire etching process. As previously reported[38], we adopted an input power of 450 W and chose argon as the precursor gas to excite the plasma at a working pressure of 0.5 Pa (at a flow rate of 10 mL·min^{-1}.

1.3 PFM and ferroelectric polarization measurements

PFM measurements were implemented on a commercial AFM (Asylum Research MFP-3D) in a resonance enhanced mode. In resonance-enhanced dual alternating current resonance tracking (DART) mode, the tip is driven by an alternating current (AC) voltage of 10 V at the resonance frequency (≈680 kHz) in lateral PFM mode, which can improve the signal-to-noise ratio. Polarization imaging at the nanoscale and local switching spectroscopy were studied with the use of conductive Pt/Ir-coated silicon probes.

2 Results and discussion

We obtained high-quality BA_2PbCl_4 crystals by using the oil bath method (Methods section). The BA_2PbCl_4 flakes were fabricated by controlling the mechanical exfoliation parameters (Fig.S1). Through a large number of experiments, we concluded that the

modified mechanical exfoliation method made it easier to fabricate large-area flakes than the conventional mechanical cleavage method (Fig.S2). Fig.1a shows that the surface of the material was very clean. By performing AFM measurements, the thickness of the sample steps was determined to be 1.7 and 3.4 nm, of which the 1.7 nm step contained two layers of benzylammonium cations and two layers of lead tetrachloride anions.

A characteristic of ferroelectrics includes a switchable spontaneous polarization. For such a microscale sample, PFM provides a convenient and non-destructive way to visualize the distribution of the polarization directions and even locally manipulate the polarization direction. In general, PFM can apply an out-of-plane electric field to manipulate polarization direction. Through the deformation of the cantilever, the piezoresponse signals in the vertical and lateral directions can be obtained, corresponding to the out-of-plane and in-plane polarizations, respectively. As previously reported, the polarization direction of BA_2PbCl_4 flakes is confined in the plane[36-37]. In recent years, examples of in-plane polarization manipulation by utilizing the trailing field have been reported[36,39]. Similarly, we utilized the trailing field to switch the in-plane polarization. When we applied a voltage of +40 V to the PFM tip and moved the tip along the dotted blue line in Fig.1c at a speed of 1 $\mu m \cdot s^{-1}$, the trailing field turned the polarization direction from right to left. The PFM amplitude image shows a clear domain wall on the left side of the dotted line (Fig. 1c), and a contrast reversal is obvious in the PFM phase image (Fig.1d). To further verify the switchability of the sample, we moved the PFM tip at the same position on the sample with a voltage of −40 V and speed of 1 $\mu m \cdot s^{-1}$. A new domain appears again to the right side of the dotted line (Fig.1e), whose polarization direction is consistent with the above domain. These results not only demonstrated robust ferroelectricity of the BA_2PbCl_4 flakes, but also provided a good platform for us to study the motion of the domain wall.

Plasma etching is a technology that is widely used in industry. Recently, layer-by-layer thinning of multilayer MoS_2 and graphene by Ar^+ plasma etching has been reported[40-41]. As a result, we used an Ar^+ plasma to etch the thickness of pristine BA_2PbCl_4 flakes. Here, the etching time for our plasma treatment was 5 min and the power was 450 W. Fig.2 (a,b) shows the optical images of the BA_2PbCl_4 sample

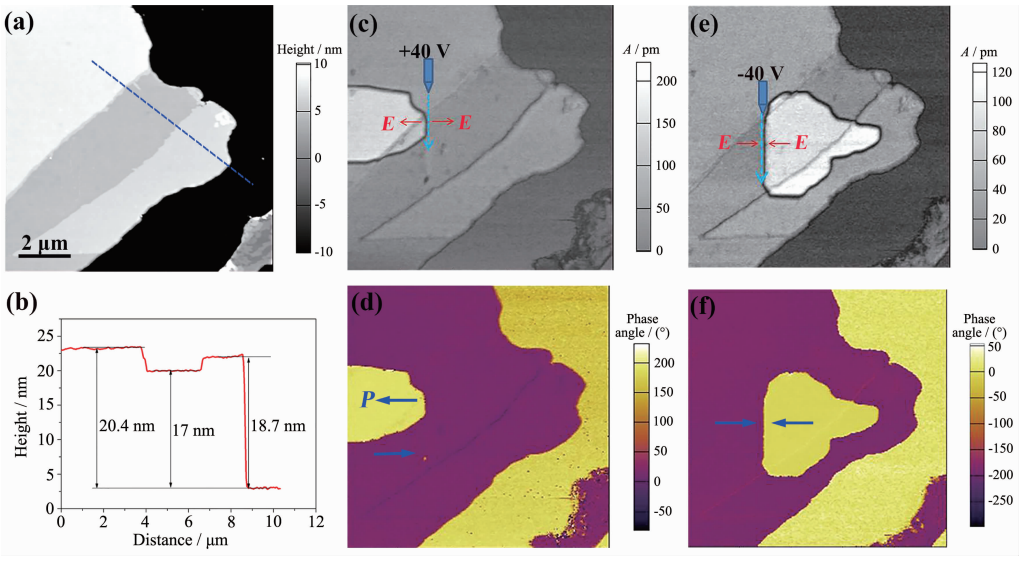

Fig.1　Room-temperature ferroelectricity in BA_2PbCl_4 flakes with different thicknesses: (a) AFM topographic image of BA_2PbCl_4 flakes prepared by the mechanical cleavage method; (b) Corresponding height profile along the dotted line in (a); (c, d) PFM amplitude and the corresponding phase images for these BA_2PbCl_4 flakes by applying +40 V to the probe; (e, f) PFM amplitude and the corresponding phase images for these BA_2PbCl_4 flakes by applying −40 V to the probe

before and after Ar^+ plasma etching, the thickness of which was determined by AFM and marked in the corresponding figure. From these two figures, we find that the shape of the sample remained unchanged after Ar^+ plasma etching. Comparing the thickness in Fig.2 (a,b), it can be seen that the etched thickness of the pristine BA_2PbCl_4 flakes with different thicknesses were different, and the change in the thickness was 97, 72, and 27 nm. In the same way, we studied 25 BA_2PbCl_4 flakes with different thicknesses. Fig.2c shows the distribution of the etching rate of the BA_2PbCl_4 flakes with different thicknesses, and the slope was 0.432. In general, the etching rate becomes saturated as the thickness of the pristine samples increases[38,42]. However, in the part of the samples that we studied, we do not see the existence of this phenomenon. These results prove that the Ar^+ plasma etching method is feasible for fabricating BA_2PbCl_4 flakes at nanometer thickness.

BA_2PbCl_4 flakes with single-unit-cell thickness were fabricated successfully after Ar^+ plasma etching, and then we used PFM to characterize the quality of this sample. Fig.3a and 3b show AFM images of the BA_2PbCl_4 flakes deposited on a 300 nm SiO_2/Si

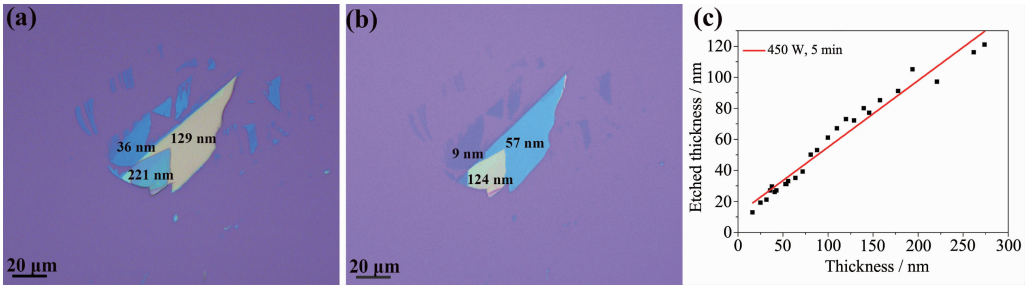

Fig.2 Ar^+ plasma etching results of BA_2PbCl_4 flakes: (a) Optical image of BA_2PbCl_4 flakes before Ar^+ etching; (b) Optical image of BA_2PbCl_4 flakes after Ar^+ plasma etching for 5 min; (c) Etched thickness as a function of pristine BA_2PbCl_4 flakes thickness at a power of 450 W

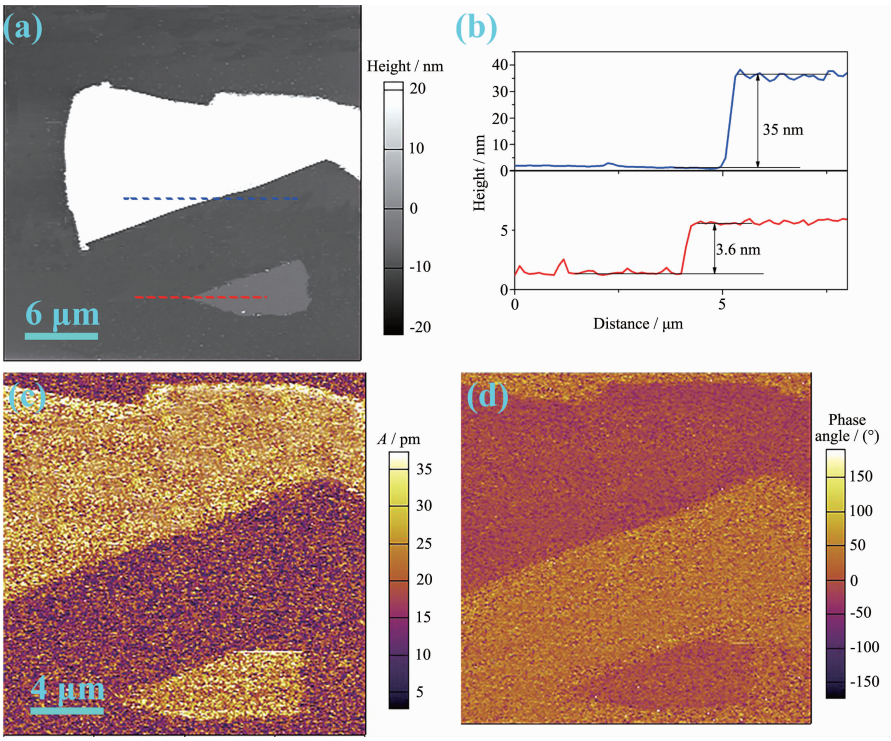

Fig.3 Room-temperature ferroelectricity in BA_2PbCl_4 flakes after Ar^+ etching: (a) AFM image of thin BA_2PbCl_4 flakes fabricated by the mechanical exfoliation method; (b) Height profiles along the corresponding solid lines in (a); (c, d) PFM amplitude and phase images of flakes fabricated by the mechanical exfoliation method

substrate and the corresponding height profiles. By comparing the undulations of the BA_2PbCl_4 flakes and the substrate, it can be seen that the BA_2PbCl_4 flakes fabricated by the method are relatively uniform as shown in Fig.3b. In previous reports, You et al.[37] prepared 4 nm thick BA_2PbCl_4 flakes with an area of approximately 2 μm^2 by traditional mechanical cleavage. It can be seen that the area of the sample with single-unit-cell thickness is approximately 20 μm^2 by optical microscopy, which demonstrates that the area of the sample prepared by the method is larger than that of the traditional mechanical cleavage method. The PFM amplitude and the corresponding phase images of the BA_2PbCl_4 flakes after Ar^+ plasma etching are shown in Fig.3(c,d), respectively. The amplitude image shows a clear distinction in the piezoresponse between the BA_2PbCl_4 flakes and the substrate, which may be due to the strong suppression of the depolarization field caused by the in-plane polarization configuration of the BA_2PbCl_4. Similar to previous observations by You et al.[37], such a finite piezoresponse strongly suggests the existence of ferroelectricity in the plasma-treated BA_2PbCl_4 flake with single-unit-cell thickness.

3 Conclusions

In summary, large-area BA_2PbCl_4 flakes fabricated by the mechanical exfoliation method were developed for the first time herein. The in-plane switchable ferroelectric polarization of 17 nm thick flakes fabricated by the method was characterized by PFM imaging, which demonstrated the existence of ferroelectricity in the BA_2PbCl_4 flakes. Thus, we demonstrated the first successful experimental method to obtain BA_2PbCl_4 flakes with single-unit-cell thickness through a combination of mechanical exfoliation and Ar^+ plasma etching, and the ferroelectricity of the sample was demonstrated by PFM at room temperature. The results presented above may accelerate the effort to break through the critical thickness of in-plane ferroelectrics by providing an efficient way to fabricate large-area, uniform BA_2PbCl_4 flakes.

Supporting information is available at http://www.wjhxxb.cn

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