Engineering Ferroelectricity and Quadruple-well State in $CuInP_2S_6$ (CIPS) via Interfacial $PbZr_{0.2}Ti_{0.8}O_3$

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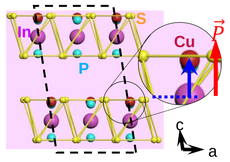
Abstract

The ferroelectric van der Waals $CuInP_2S_6$ (CIPS) possesses intriguing quadruple-well states and negative piezoelectricity. Its technological implementation has been impeded by the relatively low Curie temperature (bulk T_C~42 °C) and the lack of precise domain control. Here we show that enhanced ferroelectricity and piezoelectricity as well as controlled domain formation can be achieved in thin CIPS flakes by interfacing with ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ (PZT) films. Piezoresponse force microscopy (PFM) studies show that the polar domains in CIPS fully conform to those of underlying PZT as the flake thickness is reduced below 25 nm. The enhanced polar alignment is accompanied by a sign change in the piezoelectric coefficient d_{33}. *In situ* PFM studies reveal an enhanced T_C of ~200 ºC in thin CIPS. Density functional theory modeling of CIPS/$PbTiO_3$ reveals the critical role of interface-modulated lattice distortion, which can facilitate polar alignment in CIPS. Monte Carlo simulations show that this effect also quantitatively accounts for the enhanced T_C in CIPS. Our study provides a new material strategy for engineering the polar properties of ultrathin CIPS for developing nanoelectronic, mechanical, and energy applications.

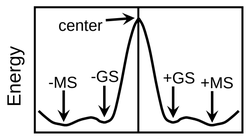
Motivation

➢ Ferroelectricity and piezoelectricity



- Large bandgap: ~2.9 eV
- Out-of-plane polarization: ~4 μC/cm²
- Negative piezoelectric coefficient d_{33}

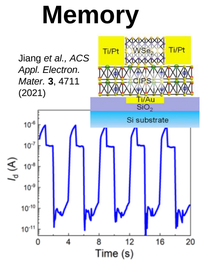
Quadruple-energy Well



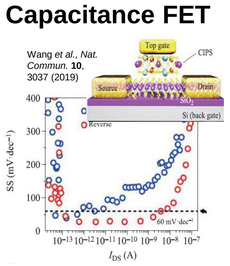
- Ground state (GS): intralayer displacement leads to negative d_{33}
- Metastable state (MS): interlayer displacement leads to positive d_{33}

➢ Potential Applications

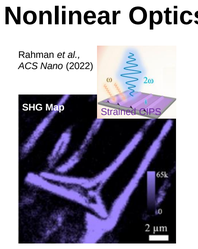
Nonvolatile Memory



Negative Capacitance FET



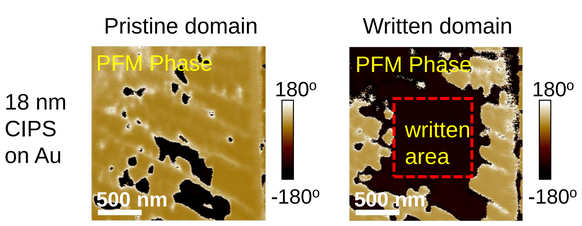
Tunable Nonlinear Optics



- ✓ Precise domain control ⇨ high density of polarization-enabled devices
- ✓ High T_C ⇨ high thermal stability

➢ Challenges

- ➢ Diffusive, rough domain walls in domain writing due to high Cu ion mobility

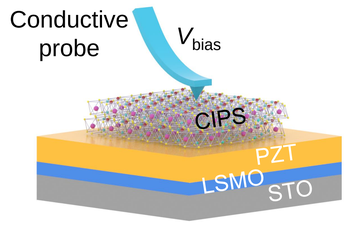


- ➢ Relatively low T_C impedes room-temperature application

Our goal: Develop a strategy to achieve controlled domain formation and enhanced T_C in CIPS

Technical Approach

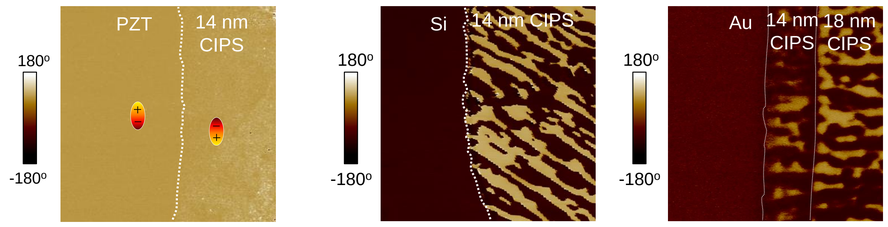
Interfacing CIPS with a ferroelectric layer



- Write domain patterns on PZT using conductive probe AFM
- Mechanical exfoliation of CIPS flakes
- Dry transfer of 6-300 nm flakes on PZT with prepatterned domain structure
- Control studies: CIPS flakes prepared on doped Si and Au

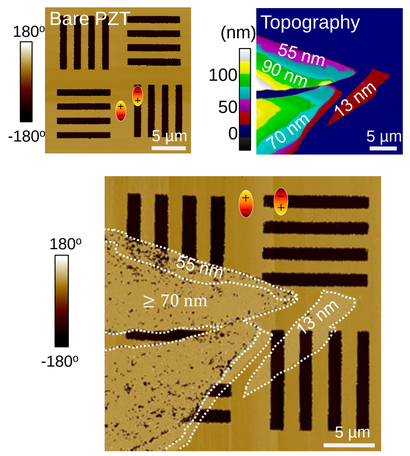
PFM Characterization

➢ Domain Formation in 14 nm CIPS on Different Substrates



- ➢ CIPS on P_{up} domain of PZT: uniform PFM phase consistent with that of PZT
- ➢ CIPS on doped Si and Au: spontaneous formation of P_{up} and P_{down} domains

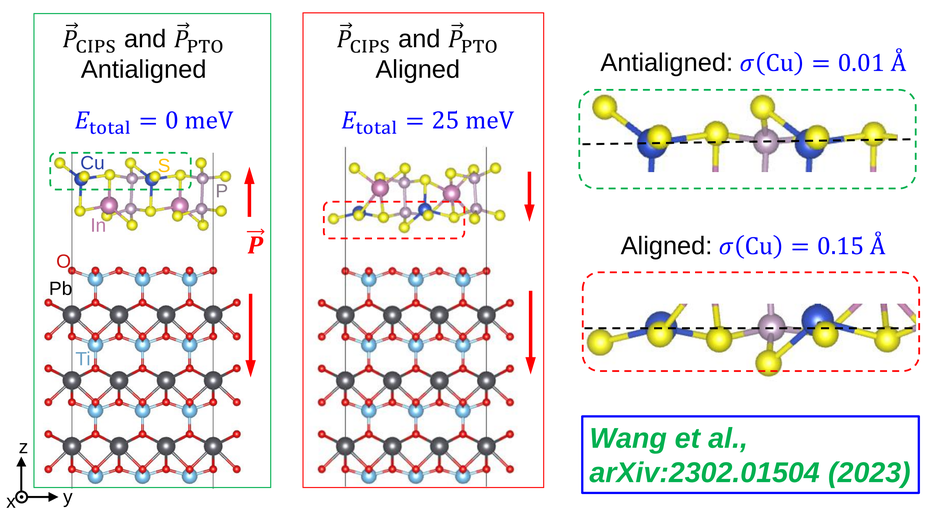
➢ Effect of CIPS Thickness on Interface Synergy between CIPS and PZT



Evolution of domain structure in CIPS with flake thickness

- 13 nm: Domain pattern conforms to that of underlying PZT
- 55 nm: Randomly distributed P_{up} and P_{down} domains start to emerge
- 70 nm and thicker: Predominantly P_{up}, regardless of the polarizations of underlying PZT
- ➢ The synergy between CIPS and PZT decays with CIPS thickness, suggesting that it is an interfacial effect

DFT Modeling of CIPS/$PbTiO_3$ Interface



Wang et al., arXiv:2302.01504 (2023)

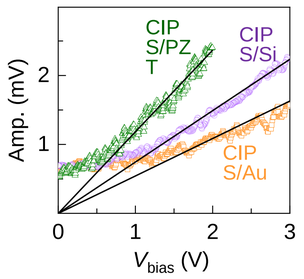
The antialigned configuration has lower energy

- Higher lattice distortion in the aligned polarization state leads to higher elastic energy cost
- Polarization antialignment is preferred, consistent with experimental observation

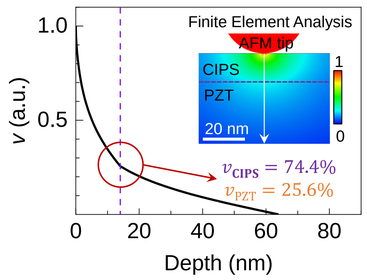
Analysis of d_{33}^{CIPS}

➢ Quantifying d_{33}^{CIPS} (*e.g.*, 14 nm CIPS)

Off-resonance PFM



Voltage across CIPS/PZT

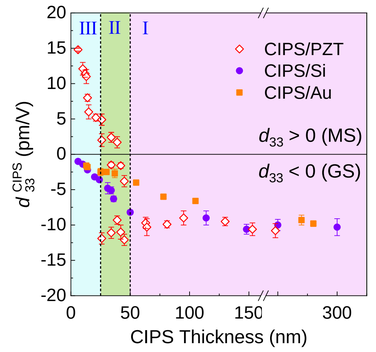


$$d_{33}^{tot} = \boxed{\frac{\partial Amp}{\partial V_{bias}}} * \frac{S}{I}$$

Polarization of CIPS and PZT antialigned

$$d_{33}^{tot} = \boxed{\nu_{PZT}} \cdot d_{33}^{PZT} - \boxed{\nu_{CIPS}} \cdot d_{33}^{CIPS}$$

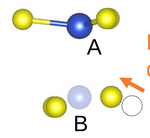
➢ Thickness Dependence of d_{33}^{CIPS}



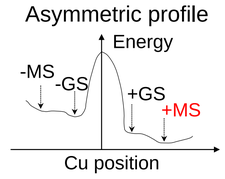
- Suppressed d_{33}^{CIPS} in thin CIPS on Si and Au
- d_{33}^{CIPS} for CIPS on PZT:
  - Ⅰ: negative d_{33}^{CIPS}
  - Ⅱ: transition region
  - Ⅲ: positive d_{33}^{CIPS}
- Enhanced d_{33}^{CIPS} in thin CIPS on PZT

➢ Mechanism for the sign change in d_{33}^{CIPS}

CIPS (P_{up}) on PTO (P_{down})



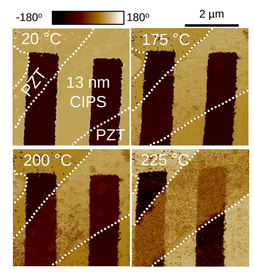
Asymmetric profile



- ➢ Interfacial lattice distortion tilts the quadruple well
- ➢ Energy barrier to MS (d_{33} > 0) is suppressed in region III

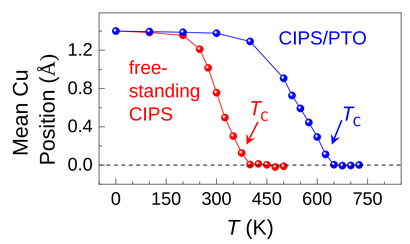
Enhanced T_C for CIPS on PZT

In-situ PFM of CIPS/PZT



- Stripe domains in CIPS disappear at 225 °C (~T_C)

Monte Carlo Simulation



- MC simulation reveals enhanced T_C ~ 650 K for CIPS on PTO, agreeing with the experimental result

Conclusion

- Domain formation in thin CIPS (< 25 nm) conforms to that in the underlying PZT
- Thin CIPS on PZT exhibits enhanced d_{33}^{CIPS} accompanied with a sign change, and T_C is enhanced by 55%
- DFT modeling reveals interfacial lattice distortion that modifies the energy profile, which can account for the enhanced ferroelectricity and piezoelectricity in CIPS

Acknowledgement

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