Scanning Probe Studies of the Piezoelectric and Ferroelectric Properties of Organic Trihalide Perovskites for Photovoltaic Applications

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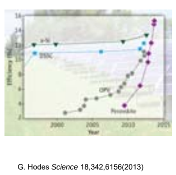
Abstract

Hybrid perovskite based solar cells, specifically $CH_3NH_3PbI_3$ ($MAPbI_3$), are drawing increasing attention recently due to their high power conversion efficiency and long photo-carrier diffusion length. It has been proposed that the excellent photovoltaic performance is related to it ferroelectric instability, whose presence in $MAPbI_3$ is a central issue in the debate. To clarify this controversy and gain a better understand of the ferroelectric property of $MAPbI_3$, we have carried out a comprehensive study of the piezoelectric and ferroelectric characteristics in the hybrid $MAPbI_3$/Pb(Zr,Ti)O_3(PZT) structure. We prepared the PZT sample (~50 nm) by off-axis radio frequency magnetron sputtering. A thin layer of $MAPbI_3$ (~100 nm) was spin coated on the PZT sample. Using piezoresponse force microscopy (PFM), we investigated the piezoelectric response of the hybrid structures. We find the piezoresponse of MAPbI3 is highly asymmetric depending on PZT's polarization, with the piezoresponse coefficient on the P_{up} domain one order larger than the P_{down} state. Signatures of possible ferroelectricity is also observed in the switching dynamics.

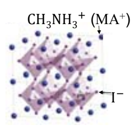
Motivation

$MAPbI_3$ is drawing increasing attention in photovoltaic applications.

- **It has been proposed that the high photovoltaic response is due to the presence of ferroelectric domains.**
- **Conclusive measurements of ferroelectricity have yet to begin**



G. Hodes *Science* 18,342,6156(2013)



S. Luo et al.Materials,9(3),123(2016)

J. Frost et al *Nano Lett.*, 2014, *14* (5)

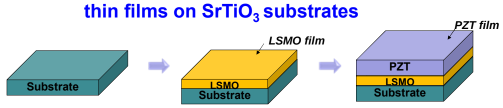
- High Power conversion efficiencies ~ 21%.
- Long photo-carrier diffusion lengths (>1 μm).

The ferroelectric domains result in internal junction that will:

- Aid separation of photoexcited carriers
- Reduce the recombination through segregation of charge carriers

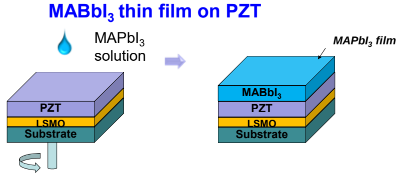
Sample Preparation

Step 1: Magnetron sputtering of epitaxial PZT thin films on $SrTiO_3$ substrates



- Sputtering of ~10 nm of (La,Sr)MnO_3 (LSMO) film on $SrTiO_3$ at 25 nm/hour
- Then sputtering of ~50 nm of PZT at 18 nm/hour
- The growth temperatures: 650 °C, 500 °C

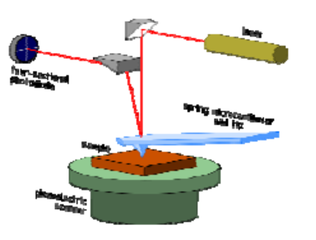
Step 2: Spin coating of the hybrid perovskite $MABbI_3$ thin film on PZT



Spin coating 5000 rpm for 30s

Bake at 100 °C for 10 min

Experimental Setup



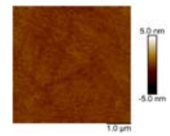
Grzegorz Wielgoszewski

- Piezoresponse Force Microscopy (PFM) uses an AC current on a Platinum-Iridium coated tip to read the converse piezoelectric effect.
- Drive amplitude: 100-500 mV
- Drive frequency: 290±20 kHz

Ferroelectric Properties of Bare PZT

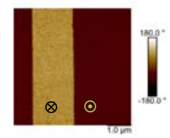
Ferroelectric Domain writing

Topography



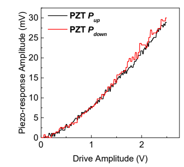
- RMS Surface Roughness of ~2 Å

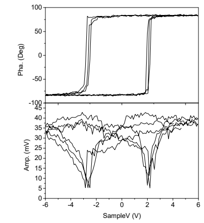
Phase image of the PFM Response



- As grown state: P_{up}
- Written Voltage P_{down}: 6V

Piezoresponse and Hysteresis Loop





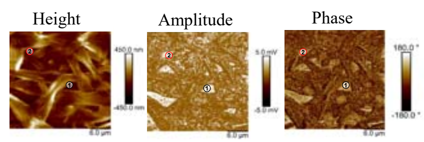
- Tip Sensitivity: 50.53 nm/V
- P_{up}:d_{33}= 25.59 pm/V
- P_{down} :d_{33}=25.43 pm/V

- Coercive Voltage for P_{up}: -2.5 V
- Coercive Voltage for P_{down}: 2 V

Relatively large piezoresponse coefficient and a symmetric hysteresis loop were observed

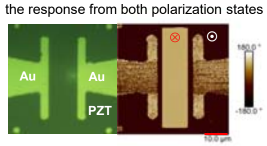
Ferroelectric Properties of $MAPbI_3$/PZT Hybrid Structure

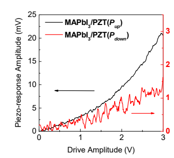
Piezo-response Measurement



- Characterization of $MAPbI_3$/PZT hybrid in the as-prepared state

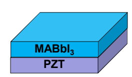
- We created domain patterns in PZT to measure the response from both polarization states





- Tip Sensitivity: 50.23 nm/V
- P_{up}: d_{33} = 10.6 pm/V
- P_{down}: d_{33} = 1.0 pm/V

Parallel plate capacitor model



$Q = C_1V_1 = C_2V_2$

$C = \frac{\epsilon A}{d}$

$\frac{V_1}{V_2} = \frac{\epsilon_2}{\epsilon_1}\frac{d_1}{d_2} = 8$

$MAPbI_3$:

- $\epsilon_1 = 25, d_1 = 100\ nm$

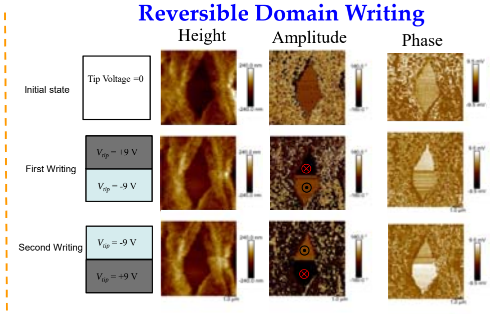
PZT:

- $\epsilon_2 = 100, d_2 = 50\ nm$

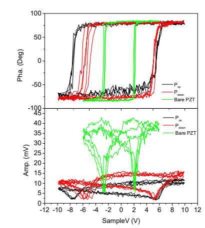
- The voltage applied to the $MAPbI_3$ is 8 times larger than the voltage going to the PZT.
- We can extract the piezoresponse of $MAPbI_3$ by subtracting the contribution from PZT, which is negligibly small.

Piezoresponse coefficient of P_{up} is one order of magnitude larger than P_{down} and through modeling this is not due to PZT

Reversible Domain Writing



➢ Polarization states are reversible and stable



- Coercive Voltage for P_{up}: -8, 6 V
- Coercive Voltage for P_{down}: -6, 5 V
- Coercive Voltage for Bare PZT: -2.5, 2 V
- Polarization of the $MAPbI_3$/PZT hybrid structure is reversible
- The hysteresis loops are asymmetric and have a much larger coercive voltage than bare PZT

- **Observed ferroelectric switch of the $MAPbI_3$/PZT hybrid structure**
- **Further experiments are required to identify the contribution of $MAPbI_3$ in the switching hysteresis loop**

Conclusion

- We have fabricated a $MaPbI_3$/PZT hybrid system and characterized its piezoelectric and ferroelectric properties using scanning probe microscopy.
- $MAPbI_3$/PZT shows enhanced piezoelectric response with high asymmetry depending on the polarization of PZT, with the piezo coefficient one order of magnitude larger for the P_{up} state.
- Clear ferroelectric switching characteristics have been observed on the hybrid system, while the contributions from the $MAPbI_3$ needs to be further investigated.

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