Emergent Electromechanical Properties of Monolayer and Few-Layer Materials

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INTRODUCTION

Piezoelectricity (defined as linear coupling between a crystal's electrical polarization and mechanical stress or strain) is present only in a small subset of engineering materials: those whose crystal structures have no center of inversion symmetry and are insulating or semiconducting. To date, these constraints have severely limited the selection of piezoelectrics available to scientists and engineers working at all length scales.

The discovery of 2D crystals has been groundbreaking because these materials possess several emergent properties that are not present in their bulk (3D) parent crystal. 2D emergent properties include: exceptional mechanical strength, graphene's exotic electronic properties, and direct band gaps in transition metal dichalcogenides.

Using density functional approaches, we have discovered that piezoelectricity is also an emergent property of many 2D crystals: BN, MoS_2, $MoSe_2$, $MoTe_2$, WS_2 and WSe_2. Whereas their bulk parent crystals are centrosymmetric, these atomically thin 2D sub-crystals are not (Fig. 1) leading to piezoelectric behavior. The magnitudes of piezoelectric coefficients are found to be comparable to those of wurtzite structure 3D materials.

The lack of piezoelectricity in the bulk crystals hints at the existence of unusual effects in the few-layer regime. We find that a curvature effect under an applied electric field, related to flexoelectricity, can occur in bilayers of some 2D materials.

SINGLE-LAYER REGIME

We have used density functional theory to compute [1] strain/stress-polarization coupling in these monolayer 2D crystals at the quantum mechanical level (Fig. 2), and have found that their piezoelectric coefficient magnitudes are par with and in some cases exceeding those of commonly used bulk piezoelectric crystals (Table 1) or doped graphene [2]. This finding establishes inorganic monolayer materials as viable candidates for expanding the horizon of sensing (e.g., displacement, force, or electric field) and actuating (e.g., switches, tweezers, or locomotive) devices in the ultrathin limit. Piezoelectric elements can be monolithically integrated with electronic elements in these semiconducting materials.

BILAYER REGIME

The bilayer stacking mode (AA') introduces an inversion center that precludes piezoelectricity. However, an entirely different mechanism for electromechanical coupling emerges. The bilayer is a cantilever-type heterostructure where one layer's strain will be opposite from that of the other (Fig. 3). This hints at the possibility of electrically controlling or sensing the curvature of a membrane that is only ~ 3 Å thick.

More detailed analysis of elasticity and the interlayer interaction using classical energy models parameterized with density functional theory reveals that such a bilayer of BN amplifies piezoelectric displacements by a factor on the order of 10^3-10^4. Radii of curvature on the order of 10 μm can thus be dynamically controlled using readily achievable electric fields of magnitude 25 V/μm.

This property of BN bilayers is also unique in that the forces and displacements it produces are reversible by changing the sign of the electric field, because the effect scales linearly with the electric field E. That is in stark contrast to carbon-based NEMS actuators that rely on electrostriction-type E^2-scaling interactions, which make the applicable forces purely attractive. Conversely, the same bilayer can also be used in a

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sensing context, where a mechanically imposed curvature leads to a measurable voltage [3].

FEW-LAYER REGIME

When extending our bilayer energy model to an arbitrary number of layers (an *N*-layer), it becomes evident that the strong curvature – electric field coupling is only present in the bilayer case. Electromechanical curvature coupling is thus an emergent property that can only be found in the ultrathin limit of a bilayer (Fig. 4).

The net strain response is zero for an even number of layers, and decays to the non-piezoelectric bulk limit as $1/N$ if N is odd [3].

ACKNOWLEDGEMENTS

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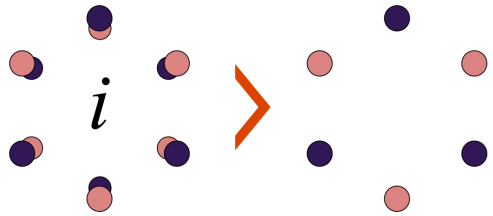

Fig. 1: Bulk BN is a stack of honeycomb 2D crystals where B and N sites alternate in neighboring layers. This bulk crystal has an inversion center. On the other hand, a single 2D monolayer has no inversion center and is thus potentially piezoelectric.

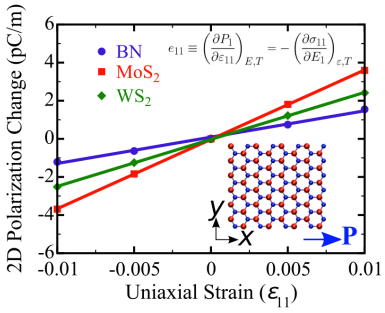

Fig. 2: Calculation of monolayer piezoelectric coefficients using density functional theory in the King-Smith/Vanderbilt/Resta polarization framework.

Table 1: Calculated piezoelectric coefficients for various 2D materials. Two commonly used 3D piezoelectrics (quartz and AlN) are added for comparison.

	e_{11} (pC/m)	d_{11} (pm/V)		e_{11} (pC/m)	d_{11} (pm/V)
BN	138	0.60	**$MoSe_2$**	392	4.72
MoS_2	364	3.73	**WSe_2**	271	2.79
WS_2	247	2.19	**$MoTe_2$**	543	9.13
quartz	**(3D)**	2.3	**AlN**	**(3D)**	5.1

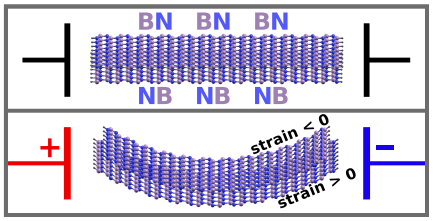

Fig. 3: The naturally occurring antiparallel stacking of piezoelectric 2D crystals enables isolation of bilayers where the constituent monolayers respond differently to the same applied electric field. This structure exhibits a curvature under an applied field.

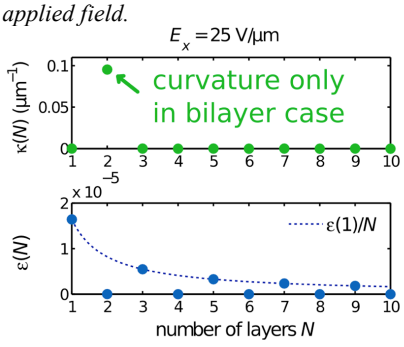

Fig. 4: Equilibrium curvature κ and average strain ε for an N-layer subjected to an electric field E_x = 25 μm. The curvature effect is an emergent property of bilayers alone, whereas the strain response will decay to the bulk limit for an odd number of layers.