Polarization Field on Edge States of Single-layered MoS$_2$

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Abstract. Operating quantum materials through the application of strong electric field holds great promise for the development of new-generation electronic and photonic technologies with currently inaccessible functionalities. The conventional way of applying gate voltage to produce sufficiently high electric field faces challenge in micro-nano level. Here, we explore polarization field of two-dimensional piezoelectric semiconductors under externally applied strain. The results suggest that the intensity of polarization field can exceed 10 MV/cm near the boundaries of single-layered MoS$_2$ ribbon. Such polarization field can trigger the metallicity-to-semiconductor (M-S) phase transition of one-dimensional edge states, and even lead to metallic bulk states. Similar phase transition can also be driven by a pure external electric field but the required intensity is in the order of MV/cm. Electric field driving the semiconducting phase of edge states presents the sensitive dependence of ribbon width but relatively robust for polarization field. This study opens a new avenue to manipulate quantum materials by high polarization field.

Keywords: Single-layered MoS$_2$, Polarization field, Edge states, Phase transition

1. Introduction
Operating on quantum materials by applying electric field makes the researches of designing faster, less energy consumption and high performance nanodevices one of the most attractive areas in nanoscale science and technology. Most researches towards these properties on demand in quantum materials usually requires sufficiently high electric field. For instance, inducing half metallicity in single-layered graphene requires the applying electric field over 10 MV/cm [1]. Polar quantum wells such as GaN/InN and ZnO/CdO can motivate topological insulator due to the presence of strong built-in electric field [2, 3]. A commonly used approach to produce electric field is to exploit gate voltage but its intensity is greatly limited by the long-distance effect with a significantly damping field. Therefore, how to obtain strong electric field in nanosystem is quite urgent.

In this work, we point out that strong piezoelectric field can be produced by externally applied strain in two-dimensional (2D) piezoelectric semiconductors. In single-layered MoS$_2$ nanoribbon, the localized field intensity can reach over 10 MV/cm near material boundaries. As an effectively modulating method, we explore the effect of strong piezoelectric field on edge states and find the phase transition from metallicity to semiconductor. In comparison with pure electric-field modulation, piezoelectric field behaves robustly to the variation of ribbon width and has greater tunability in semiconductor phase.
2. Polarization Field in Single-layered MoS$_2$

Analogous to graphene, single-layered MoS$_2$ has hexagonal honeycomb structure and its unit cell is shown in figure 1(a). When a tensile (compressive) strain is imposed along the armchair direction, polarization vector $\mathbf{P}$ is induced and its direction points from S (Mo) to Mo (S) site.

In piezoelectric semiconductors such as ZnO, GaN and single-layered MoS$_2$, strain-induced piezoelectric charges are mainly distributed at material surfaces or boundaries, leading to the localization of piezoelectrically polarized field. This piezoelectric field can effectively control the photoelectric and transport property of charged carriers in nanodevices [4]. For two-dimensional piezoelectric materials where its boundaries can be viewed as one-dimensional (1D) wires, piezoelectric field can be approximately solved from the model of 1D charged wires or an electric dipole [5], as shown in figure 1(b). According to Gauss theorem, the piezoelectric field is given by

$$ E_{\text{piezo}} = \frac{e_{11}s_{11}}{2\varepsilon_r\varepsilon_0} \left( \frac{1}{x} + \frac{1}{W - x} \right) $$

(1)

where $e_{11}$ and $s_{11}$ are the piezoelectric coefficient and applied stress along armchair direction, $\varepsilon_r$ and $\varepsilon_0$ are the relative and vacuum dielectric constant, $W$ is the ribbon width and $x$ is the distance away from the zigzag edge. The piezoelectric potential is then solved as

$$ V_{\text{piezo}} = \frac{e_{11}s_{11}}{2\varepsilon_r\varepsilon_0} \ln \left| \frac{x}{W - x} \right| $$

(2)

This logarithmic dependence of piezoelectric potential generated by polarization charges is also reported in some 2D systems such as monolayer SnSe [6], II-IV, III-V and IV-IV honeycomb insulators [7] and the interfacial dipole in graphene/h-BN lateral heterostructures [8].

![Figure 1](image)

Figure 1. (a) The piezoelectric property of MoS$_2$. Polarization $\mathbf{P}$ arises from the center deviation of anions and cations under an externally applied strain. (b) The distribution of electrical field and potential for an electric dipole. (c) The distribution of piezoelectric field and potential for a MoS$_2$ ribbon with 6 nm width under strain 1%.

Figure 1(c) shows piezoelectric field and potential distribution across MoS$_2$ ribbon under externally applied strain $s_{11} = 1\%$ and the ribbon width $W = 6$ nm. Piezoelectric field becomes strong near the boundaries but sharply declines approaching the middle region. Recent experimental results in
two-dimensional WSe2/MoS2 lateral heterostructure have also indicated such localization of piezoelectric field at interfaces [9], as shown in figure 2. Theoretical results based on first-principle calculation have also found strong piezoelectric field at the interfacial domain in 2D Graphene/h-BN lateral heterojunction [10].

Figure 2. The distribution of piezoelectric field near the interface of WSe2/MoS2 heterostructure. The circle is obtained from experimental results in Ref. [9] and the solid line is calculated from the formula $E = 0.18 / d$. The insert shows the piezoelectric charges in the interface of lateral heterostructure.

3. Polarization Field-driven Phase Transition of Edge States

1D metallic edge modes can be observed at the smooth boundaries of the single-layered TMDs [11]. Edge states of single-layered MoS2 can be well captured by Slater-Koster tight-binding model. Under six basis $[d_{3z^2-r^2}, d_{x^2-y^2}, d_{xy}, p^x, p^y, p^z]$, the tight-binding Hamiltonian is presented by [12]

$$H = \sum_{i,\mu\nu} \varepsilon_{\mu,\nu} c_{i,\mu}^\dagger c_{i,\nu} + \sum_{i,j,\mu\nu} [t_{i,j,\mu\nu} c_{i,\mu}^\dagger c_{j,\nu} + \text{H.c.}]$$

(3)

where $c_{i,\mu}^\dagger$ ($c_{i,\mu}$) is the creation (annihilation) operator of an electron in unit cell $i$ located in $\mu$ atomic orbital. $\varepsilon_{\mu,\nu}$ is the onsite energies of the atoms and $t_{i,j,\mu\nu}$ is the hopping energies between two nearest atoms. H.c. is the operator ensuring that the tight-binding Hamiltonian is Hermitian. All parameters in Eq. (3) are found in Ref [12]. Deformation potential can be well described by changing the hopping energy, following Ref [13].

Figure 3 calculates the electronic structures of 24-atoms zigzag MoS2 nanoribbon (with width 4.4 nm) under different strains. At no strain, edge states are metallic, as seen in figure 3(a). Figure 3(b) shows that at a critical strain $\delta_{11} = 2.5\%$, conduction and valence edge states start to contact at $ak_s = \pi$. Further increasing the strain, the gap is opened and edge states become semiconducting in figure 3(c). Such metallicity-to-semiconductor phase transition induced by piezoelectric field has also been reported in recent studies in quantum piezotronic devices [14, 15].
Figure 3. Band dispersion of monolayer MoS₂ with width 4.4 nm under armchair-directional strain (a) 0, (b) 2.5% and (c) 4.0%.

Figure 4(a) shows the edge-state gap as a function of ribbon width $W$ and strain $s_{11}$. There are three phase regions: metallic edge state (MES), semiconducting edge state (SES) and metallic bulk state (MBS). In the MES under a small strain, edge states are commonly metallic and bulk states are semiconducting. With the ribbon width increasing, the critical strain occurring metallicity-to-semiconductor phase transition of edge states maintains almost unchanged at $s_{11} = 2.0\%$.

In the SES, the gap increases first and then decreases to zero with the strain growing. The increasing gap by strain is the result of the rising piezoelectric field, whereas the decreasing of the gap is due to the reduced bulk gap by the combined effect of piezoelectric field and deformation potential. Under a large strain, edge states drown in the metallic bulk states, thus giving rise to zero gap in the MBS.

As a comparison, we also study edge states under the influence of an externally applied uniform electric field in figure 4(b). It requires a high electric field (in the order of MV/cm) to open a gap of edge states. As the ribbon width increases, the region of the SES sharply shrinks. This is because of potential drop of two terminated sides which grows almost linearly with the width $V_{\text{drop}} = E_{\text{ext}} W$. Electric field to close bulk gap $\Delta_{\text{bulk}}$ is approximately $E_{\text{ext}} \Delta_{\text{bulk}} / W$, which is rapidly reduced with the increase of ribbon width $W$.

Figure 4. The contour of edge-state gap versus (a) ribbon width and strain and (b) ribbon width and externally applied electric field.
4. Conclusion

We have studied the polarization field of two-dimensional piezoelectric semiconductor materials MoS$_2$ and its tuning on edge states. The results suggest that in zigzag MoS$_2$ nanoribbon, the induced piezoelectric field is comparatively strong near the boundaries and sharply weakens away from the boundaries, behaving interestingly local distribution. As a typical example for illustrating the operating of quantum states, we further demonstrate the difference of edge-state phase transition between by strain-induced polarization field and by pure electric field. Inducing a phase transition from metallic to semiconductor in edge states requires much strong electric field exceeding MV/cm. However, this transition can be expediently obtained by a small strain. Moreover, piezoelectric field behaves robustly to the change of ribbon width, and has greater tunability in semiconductor phase of edge states.

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