Resonant Tunneling through Discrete Quantum States in Stacked Atomic-Layered MoS$_2$

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ABSTRACT: Two-dimensional crystals can be assembled into three-dimensional stacks with atomic layer precision, which have already shown plenty of fascinating physical phenomena and been used for prototype vertical-field-effect-transistors.$^{1,2}$ In this work, interlayer electron tunneling in stacked high-quality crystalline MoS$_2$ films were investigated. A trilayered MoS$_2$ film was sandwiched between top and bottom electrodes with an adjacent bottom gate, and the discrete energy levels in each layer could be tuned by bias and gate voltages. When the discrete energy levels aligned, a resonant tunneling peak appeared in the current–voltage characteristics. The peak position shifts linearly with perpendicular magnetic field, indicating formation of Landau levels. From this linear dependence, the effective mass and Fermi velocity are determined and are confirmed by electronic structure calculations. These fundamental parameters are useful for exploitation of its unique properties.

KEYWORDS: Metal transition dichalcogenide, MoS$_2$, interlayer electron transport, resonant tunneling, discrete energy levels, nanopore structure

Molybdenum disulfide (MoS$_2$) is a prototypical transition metal dichalcogenide. It has a layered structure wherein molybdenum atoms are sandwiched between the layers of sulfur atoms in a hexagonal arrangement. Atomic MoS$_2$ sheet is a semiconductor with large bandgap. Similar to graphene, single layer MoS$_2$ possesses unique properties such as high transparency and two-dimensional (2D) flexible geometry and has become an emerging material in the field of nanoelectronics.$^{3−10}$ In multilayer structures, the interlayer interaction can play an important role in determining electronic properties. In the case of few-layer graphene, the interlayer coupling can modify the subband curvature, leading to the opening of a subband spacing or energy gap.$^{17−21}$ Experimental studies on the interlayer electron transferring in graphene systems were conducted and exhibited interesting transport behavior.$^{22,23}$ In the case of multilayer MoS$_2$, the interlayer coupling arises from overlapping of electron wave function due to the small separation between sulfide sheets. Consequently, the bandgap of the multilayer structure is predicted to be tunable by an electric field.$^{24}$ Although lateral transport properties of few-layer MoS$_2$ have been studied experimentally,$^{8−15}$ perpendicular-to-plane electrical transport has not been investigated. Experimental study on interlayer electron transferring in MoS$_2$ systems should reveal useful information needed for the development of multilayered electronics.

In this work, we report perpendicular electron transport through a highly crystalline trilayer MoS$_2$ structure in nanometer area. The interlayer tunneling current was found to be modulated by transverse electric fields as well as perpendicular magnetic fields. Our experiment provided evidence of inter-MoS$_2$ layer charge tunneling and suggested a wave function overlap between the sulfide atomic layers of the two stacked MoS$_2$ layers. Furthermore, the current–voltage ($I−V$) characteristics exhibited a resonant peak structure, suggesting presence of quantized energy levels in the MoS$_2$ sheets. The peak position shifted linearly with the perpendicular applied magnetic field, indicating formation of Landau levels. From this dependence, the effective mass and Fermi velocity were determined. The effective mass was found to be much smaller than the predicated value for single MoS$_2$ layers. Electronic structure calculation was performed to confirm the experimental results.

High quality atomic-layered MoS$_2$ films were synthesized by the following processes.$^{25}$ Cleaned sapphire substrates were immersed into 1.25 wt % of (NH$_4$)$_2$MoS$_4$ and dimethylformamide (DMF) solution and then slowly pulled out to form thin
(NH₄)₂MoS₄ films on the substrate surface. In general, few-layer MoS₂ sheets could be obtained using diluted precursor solution and with a fast dip-coating process. Residual solvents and other contaminations were removed in 1 Torr Ar/H₂ gas mixture (flow rate ratio = 4:1) at for 500 °C for 1 h. Subsequently, the specimen were subjected to a second annealing process in 500 Torr Ar/S gas mixture at 1000 °C for 30 min. The added sulfur helped to improve the crystalline annealing process in 500 Torr Ar/S gas mixture (fl).

Figure 1a shows a transmission electron microscopy (TEM) image of the synthesized MoS₂ sheets, which reveals periodic atom arrangement of highly crystalline trilayer MoS₂ films. As shown in Figure 1b, the three layers can be clearly identified in the curled edge of a free-hanging trilayer. Figure 1c displays the selected area electron diffraction (SAED) pattern showing three sets of hexagonal lattice structure, indicating that misorientation may exist at some places. Diffraction patterns (not shown) indicated that the crystalline domain size is greater than 250 nm. It is also noted from TEM-based energy dispersive spectroscopy (TEM-EDS) analysis (Figure 1d) that the atomic percentage ratio between Mo and S is 1:2.

The trilayer MoS₂ films were then made into electronic devices by using the following procedures. Silicon nitride (Si₃N₄) membrane chips with millimeter-sized Au contact pad on the front-side for electrical measurements were made on 500 μm thick silicon substrates by standard photolithography and anisotropic KOH etching. Electron-beam lithography and reactive-ion etching were then employed to create a nanopore on the membrane. The pore was then surrounded by a 24 nm thick aluminum (Al) gate-electrode, which is covered by an 8 nm thick aluminum oxide (Al₂O₃) insulating layer. Because of these coating layers, the diameter of final pore on the Si₃N₄ membrane shrank. As shown in the inset of Figure 2a, the diameter of pore in Device 1 is about 28 nm. The diameters of pores in Device 2 and 3 are 44 and 72 nm, respectively, as shown in Supporting Information. The as-grown trilayer MoS₂ was then transferred to the top of nanopore on membrane. Prior to the transferring, the sapphire-caped trilayer MoS₂ sheets were spin-coated with PMMA and then immersed into NaOH solution to etch away sapphire. The PMMA-caped MoS₂ was first cleaned by deionized water and placed on membrane surface to cover the nanopore. After removing PMMA, the trilayer MoS₂ surface was further cleaned by chloroform. Figure 2b displays Raman spectra of the transferred MoS₂ film at the membrane area. The film exhibits two Raman characteristic peaks at 383.2 and 405.4 cm⁻¹, corresponding to E₁g and A₁g modes, respectively. The energy difference between two peaks is 22.2 cm⁻¹, indicating that the MoS₂ film has trilayer structure, as reported in the TEM analysis in Figure 1. After transferring of the trilayer MoS₂, Au/Ti films are subsequently thermally evaporated onto the both sides of the chip to form top and bottom electrodes. Ti is chosen as the contact metal because the work function of Ti (~4.3 eV) is very close to the electron affinity of thin-layer MoS₂ (~4.2 eV), and a good Ohmic contact between them is expected. As schematically illustrated in Figure 2c,d, the completed device consists of a trilayer-MoS₂, laid on top of the gated nanopore and sandwiched between top and bottom electrodes. The overlapping of electron wave functions between layered MoS₂ enables interlayer charge transfer, just like that in few-layer graphene. Under a bias source-drain voltage V_{ds}, this charge transfer yield a perpendicular current I. This perpendicular current through the trilayer MoS₂ will be confined on one side by a nanopore on a Si₃N₄ membrane. In addition, capacitive coupling exists between the bottom gate electrode and each MoS₂ layers. This coupling enables gate-modulation of the carrier concentration in MoS₂ layers, making the device a vertical field-effect-transistor. Details of nanopore fabrication procedure and transfer process can be found in ref 28 and in Supporting Information (Figure S1). All the low-temperature electrical measurements were carefully conducted using a homemade current—voltage amplifier with completely symmetric circuit for best common-mode noise rejection.

**Figure 2.** (a) Optical microscopy image of a Si₃N₄ membrane chip coated with transferred trilayer MoS₂. The inset is an SEM image of Device 1 showing a nanopore made on Si₃N₄ membrane. (b) Raman spectra for the transferred trilayer MoS₂ on the membrane. (c) Schematic illustration of the nanopore device with the trilayer MoS₂ sandwiched between the top and bottom electrodes. (d) A cross-sectional drawing of the trilayer MoS₂ device structure at the nanopore area.
On the basis of the device geometry shown in Figure 2d, a circuit model displayed in Figure 3a is proposed, in which the three MoS$_2$ layers from top to bottom are denoted as L1, L2, and L3. As illustrated in Figure 2d, the top contact area between Ti/Au and MoS$_2$ is about 40 000 times larger than that of the bottom contact; the latter is defined by the nanopore. This difference in the contact area results in a large difference in the contact resistance. This, together with the gated transistor circuit, gives rise to the rectification current–voltage ($I$–$V_b$) characteristics shown in Figures 3b and 3c. Similar types of structure–asymmetry induced rectification behavior are reported for not only nanopore devices, but also nanowire devices with different contact areas. Figure 3b and the inset show gate modulation of current, clearly displaying n-type behavior. Throughout this work, the carrier concentration in MoS$_2$ layers is depleted to a low value by displaying n-type behavior. Throughout this work, the carrier concentration in MoS$_2$ layers is depleted to a low value by displaying n-type behavior.

Figure 3. (a) The proposed model of the gated-trilayer MoS$_2$ device sandwiched between top (T) and bottom (B) electrodes. (b) $I$–$V_b$ curves of Device 3 at gate voltages varying from −1.5 V (left-most green curve) to −0.5 V (right-most black curve) with a step of 0.1 V at 60 K. Inset shows $I$–$V_b$ characteristics at $V_g$ = 1 V (black), 0.9 V (red), and 0.8 V (blue), indicating that the MoS$_2$ trilayer is of n-type. (c) $I$–$V_g$ curve of Device 1 at gate voltage of 0.1 V measured at 3 K. The inset displays a magnified $I$–$V_b$ at resonant tunneling peak around 512 mV. The very smeared current plateau at $V_b$ ~ 400 mV can probably be explained by tunneling through broadened levels. (d) Schematic illustration of the potential diagram for the energy level alignment at which the current reaches maximum value. As gate or drain voltage is tuned away, these energy levels are not aligned and the tunneling current decreases.

Figure 4. (a) $G_f$ versus $V_b$ curves of Device 3 at gate voltages of −0.7 V (black, bottom), −0.4 V (blue), 2 V (red), and 3 V (green, top) at 30 K. (b) Resonant peak position (in $V_b$) as a function of gate voltage. Red dashed line is a guide to the eye.

are not aligned and the differential conductance $G_d = dl/dV_b$ drops. Shown in Figure 4b is the linear shift of the conductance peak position with respect to $V_b$ and $V_f$ values. This linear shift is commonly observed in resonant tunneling transistors.

Figure 5a and the inset show how the resonant peak shifts in the presence of perpendicular magnetic fields, which is a manifestation of Landau level shift given by $\Delta E = \hbar \omega_c / e B$, where $e$, $\hbar$, $B$, $\omega_c$, and $m^*$ are the elementary charge, Planck’s constant, magnetic field, cyclotron frequency, and the effective mass, respectively. As displayed in Figure 5b for Device 1, for magnetic fields higher than 3.5 T the resonant peak position shifts linearly with magnetic field. From this
linear dependence, the effective mass is determined to be 0.047 $m_e$ with $m_e$ the electron rest mass. The onset magnet field ($B_{\text{onset}} = 3.5$ T) corresponds to the largest circle that allows formation of cyclotron motion, which has a cyclotron frequency $\omega_{c,\text{min}}$ of $1.31 \times 10^{13}$ rad/s. In view of our nanopore structure, it is reasonable that the cyclotron motion can exist only inside the nanopore. Outside the pore, the cyclotron motion is quenched by the interaction between MoS$_2$ and underneath Al$_2$O$_3$ insulating layer. By assuming a cyclotron radius $r_c$ equal to the nanopore radius (14 nm for Device 1), the Fermi velocity $v_F = r_c \omega_{c,\text{min}}$ is determined to be $0.183 \times 10^6$ m/s. As shown in Figure 5c,d, Devices 2 and 3 also exhibit similar linear dependence, the $e^*$ from each other. This deviation can possibly be attributed to the MoS$_2$ trilayers are performed, and the results are described in the Supporting Information. The calculated average Fermi velocities are 0.19 $\times 10^6$ and 0.15 $\times 10^6$ m/s, respectively, whereas the effective masses are estimated to be about 0.047 and 0.032 $m_e$ respectively. These values fully support our experimental findings. Also notice that the calculated $m^*\nu_F$ products are about 0.007 (in unit of $m_e^*m_e^*$), which agree reasonably with the experimental value of 0.011 obtained from the slope in Figure 5e.

With the knowledge of the effective mass, the mean energy level spacing estimated by $\Delta E = (1/\pi)(h^2/m^*)(\pi^2/m^*r^2) = (h^2/m^*r^2)$ for devices 1, 2, and 3 are about 8 meV (137 K), 3.24 mV (56 K) and 1.2 mV (21 K), respectively. These values are much greater than the thermal energy at 3 K, ensuring tunneling through a discrete level. The randomly embedded charge traps in the Al$_2$O$_3$/MoS$_2$ interface generate strong potential fluctuations, which lead to localization of carriers in the MoS$_2$ outside the nanopore, giving rise to insulating behavior at low temperatures. Because the free carriers are confined in the nanopore area, the energy levels are quantized. At temperatures higher than 40 K the conductive behavior in the MoS$_2$ outside the pore is recovered, and the carriers inside the pore area are thus delocalized. This transition from low-temperature localized state to high-temperature extended state can be clearly seen in Figure 6 in which the resonant peaks from 10 to 40 K are gradually smeared. As shown in Figure S3 in Supporting Information, similar behaviors were observed in

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which is in reasonable agreement with the average value of 0.028 $m_e$ obtained from Table 1. Despite of this consistency, we note that these experimental values are one order smaller than the theoretical value of 0.5 $m_e$ for MoS$_2$ monolayers. To support the obtained experimental values first-principle calculations for effective mass in MoS$_2$ monolayers are performed, and the results are described in the Supporting Information. The calculated average Fermi velocities are 0.19 $\times 10^6$ and 0.15 $\times 10^6$ m/s, respectively, whereas the effective masses are estimated to be about 0.047 and 0.032 $m_e$ respectively. These values fully support our experimental findings. Also notice that the calculated $m^*\nu_F$ products are about 0.007 (in unit of $m_e^*m_e^*$), which agree reasonably with the experimental value of 0.011 obtained from the slope in Figure 5e.

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Figure 6. $I-V_t$ characteristics at temperatures from 40 K (black curve) to 10 K (purple curve) with a step of 5 K in Device 1. Note that the resonant peaks become apparent at low temperatures.

Devices 2 and 3. Furthermore, because the MoS$_2$ trilayer are likely to stack with random orientations (see Figure 1c), the wave-vector of tunneling electrons may vary from one layer to the other due to different orientations in the two-dimensional Brillouin Zone. The requirement that transverse momentum of tunneling electrons has to be conserved in the resonant tunneling process implies that the momentum-conserved interlayer transport can take place at different $k$-points of the two involving layers.

In conclusion, interlayer resonant tunneling between high-quality MoS$_2$ sheets was investigated. In the presence of a high-perpendicular magnetic field, the resonant tunneling peak position shifts linearly with the field strength, indicating formation of Landau levels. From the onset field and the slope of this linear dependence, Fermi velocity and the effective mass were determined, respectively, and these values were confirmed by band-structure calculations. The information from this expedition will pave the way for the development of MoS$_2$ electronics.

**ASSOCIATED CONTENT**

Supporting Information

Procedures for transferring as-grown MoS$_2$ sheets, additional transport characteristics for Devices 2 and 3, and band structure calculation for MoS$_2$ trilayer are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


