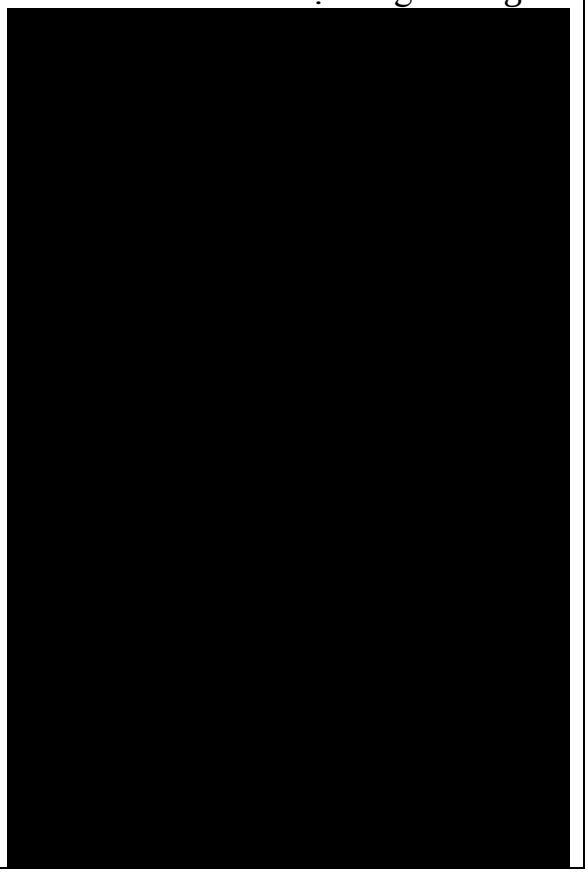
Tunable Bandgap in Silicene and Germanene checked 3/4 Supporting Information ABSTRACT: By using ab initio calculations, we predict that a vertical electric field is able to open a band gap in semimetallic single-layer buckled silicene and germanene. The sizes of the band gap in both silicene and germanene increase linearly with the electric field strength. Ab initio quantum transport simulation of a dual-gated silicene field effect transistor confirms that the vertical electric field opens a transport gap, and a significant switching effect by an applied gate voltage is also observed. Therefore, biased single-layer silicene and germanene can work effectively at room temperature as field effect transistors. Graphene has attracted great interest recently for its exceptional electronic properties.1 -4 For instance, its charge carriers are massless Dirac fermions, leading to a mobility up to 15 000 cm2 V-1 s-1 for graphene on SiO2 substrate and 200 000 cm2 V-1 s-1 for suspended sample.1-4 However, the promising application of graphene in present electronic devices, like field effect transistor (FET), still relies on the opening and controlling of the band gap. Although a band gap is opened in bilayer and multilayer graphene under an external vertical electric field due to the inversion symmetry breaking,5 9 monolayer graphene remains zero-gap semimetallic because its two sub-lattices remain	Độ rộng vùng cấm tùy chỉnh trong Silicene và Germanene Tunable: tùy chỉnh, thay đổi được Thông tin hỗ trợ TÓM TẮT: Thông qua việc sử dụng tính toán ab initio (tính toán dựa trên nguyên lý đầu), chúng tôi dự đoán rằng một trường dọc có thể mở vùng cấm trong silicene và germanene dạng cong đơn lớp bán kim loại. Kích thước của độ rộng vùng cấm trong cả silicene và germanene tăng tuyến tính theo cường độ điện trường. Mô phỏng vận chuyển lượng tử Ab initio của transistor hiệu ứng trường bằng vật liệu silicene hai cổng khẳng định rằng trường điện dọc mở ra một khe vận chuyển và chúng tôi cũng đã quan sát được hiệu ứng chuyển mạch rõ nét khi áp vào một điện áp cổng. Do đó, silicene và germanene đơn lớp phân cực có thể hoạt động hiệu quả ở nhiệt độ phòng như các transistor hiệu ứng trường . 

equivalent under an external vertical electric field. Consequently, biased monolayer graphene cannot be operated effectively as a FET at room temperature. Other group IV elements, such as silicon and germanium, also have stable honeycomb monolayers (namely silicene and germanene).10'11 Synthesis of pristine,12 Mg-doped13 and hydrogenated14 silicene, and pristine silicene nanoribbon15 have been reported. Unlike planar graphene monolayers, the most stable silicene and germanene monolayers prefer a low-buckled (LB) structure (silicene and germanene referred to in the following are those with LB structure). The electronic structures of the silicene and germanene are quite similar to that of graphene.10'11 Namely, silicene and germanene are zero-gap semimetallic, and their charge carriers are also massless fermions because their n and n* bands are linear at the Fermi level (Ef). When a vertical electric field is applied, the atoms in a buckled structure are no longer equivalent, and a band gap opening may become possible in silicene and germanene. If so, one can fabricate an FET operating at room temperature out of pure silicene and germanene.

In this Letter, we investigate the effects of a vertical electric field on silicene and germanene by means of the density functional theory (DFT) and the nonequilibrium Green's

function (NEGF) method.

A band gap is unambiguously opened, and its size and the effective carrier mass increase linearly with the electric field strength. The effects ofthe vertical electric field on the transport properties of silicene are subsequently examined by fabricating a prototype of dual-gated silicene FET. A transport gap induced by perpendicular electric field is found, accompanied by significant switching effects by gate voltage.

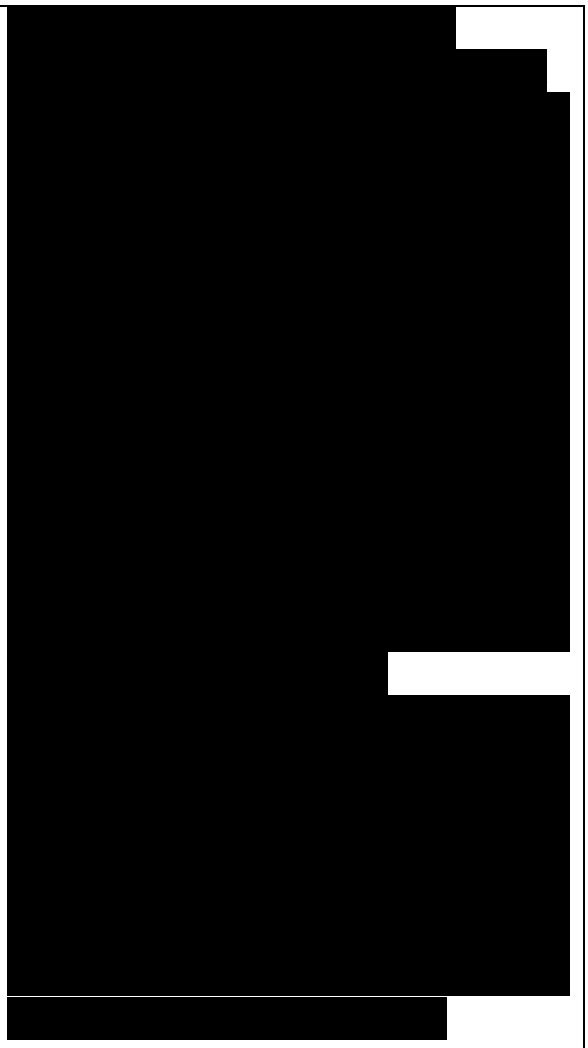
Geometry optimization and electronic structure are calculated by using an all-electron double numerical atomic basis set plus polarization (DNP), as implemented in the Dmol3 package. A 32 X 32 X 1 Monkhorst-Pack17 k-points grid is used in the first Brillouin zone sampling. A vacuum space of 20 A is placed to avoid interaction between the monolayer and its periodic images. Both the atomic positions and lattice constant are relaxed. Transportation properties are calculated by the DFT coupled with NGEF formalism implemented in the ATK 11.2 package.18 20 Both single-Z (SZ) and double-Z plus polarization (DZP) basis sets are employed. The k-points of the electrodes and central region, which are generated by the Monkhorst-Pack scheme as well, are set to 1 X 300 X 300 and 1 X 300 X 1, respectively. The temperature is set to 300 K. The current is calculated by using the Landauer-Buttiker formula:21

where Tvg(E, Vbias) is the transmission probability at a given gate voltage Vg and bias voltage

Vbias, fL/R the Fermi-Dirac

Figure 1. (a) Top and side view of silicene monolayer. The primitive cell is denoted by the red rhombus. The two equivalent atoms in silicene, labeled as A and B, respectively, have a corrugated arrangement. The structure of germanene is almost the same, except for a slightly larger lattice constant and buckling distance. (b) Buckling distance A of silicene and germanene as a function of calculated at the GGA/ DNP level. The left scale is for silicene, and the right one is for germanene.

Figure 2. Band structures of (a—c) silicene and (d—f) germanene around Ef at three different vertical electric fields calculated at the GGA/ DNP level. Inset in (a) and (d): Band structures in the first Brillouin zone at E^ = 0. The Fermi level or the valence band top is set to zero.



distribution function for the left (L)/right (R) electrode, and ^L/^Rthe electrochemical potential of the L/R electrode. Effects of gate are calculated by solving the Poisson equation self- consistently instead of simply lifting the central region's chem-ical potential. A generalized gradient approximation (GGA) to the exchange—correlation functional, of the Perdew—Burke— Ernzerhof (PBE) form,22 is used throughout this paper, unless otherwise specified.

Figure 3. (a) Band gap, (b) Mulliken charge transferred from one equivalent atom to the other, and (c) effective mass of electron at the conduction band bottom along the

KF and MK directions of silicene and germanene as a function of vertical electric field calculated at the GGA/ DNP level. The coupling coefficient of nearest neighbors in the TB model is set to 1.7 eV in silicene and 2.0 eV in germanene.

The optimized electric field free silicene (shown in Figure 1a) and germanene at the GGA/DNP level have lattice constants of a = 3.866 and 4.063 A, respectively. The corresponding buckling distances are A = 0.460 and 0.676 A, respectively. These structural parameters are in good agreement with previous works.10,11,23 As displayed in Figure 1b, the A value increases monotonically and nonlinearly with E^ after the application of a vertical electric field, with an increment of 3%/0.2% at E± = 0.51 V/A and 8%/0.8% at E± = 1.03 V/Ain silicene/germanene. The changes in the lattice constant a are less than 0.2% in both silicene and germanene under E± = 0—1.03 V/A. Figure 2a—f shows the band structures of silicene and germanene under three different electric field E^. Their conduction and valence bands touch linearly at the K point when E± = 0; thus, both silicene and germanene are semimetals with zero gap and zero effective mass. However, when finite E^ is applied to silicene and germanene, a direct band gap is opened at the K point. The opened band gap is Eg = 0.08/0.06 eV for silicene/germanene under E± = 0.51 V/A and doubled under E^ = 1.03 V/A. The finer response of the band structure to E± of silicene is provided in Figure S1, Supporting

Information. As shown in Figure 3a, the opened band gap increases linearly with E^ and surpasses the room temperature scale (0.026 eV) at E± = 0.16 V/A. The electric field required to open a gap of 0.16 eV in silicene and germanene is greater than that in bilayer and multilayer graphene by about an order of magnitude, but the band gaps in the latter increase nonlinearly with E^ and are saturated around E^ = 0.1 V/A.7—9 Considering the sizable underestimation of the band gap in conventional DFT for a low-dimensional semiconductor, , the real band gaps in silicene and germanene should be significantly greater than the GGA/DNP ones. The MIN basis set yields a 4% larger lattice constant and 60—70% larger buckling (see Figure S2a, Supporting Information) than the DNP results and other theoretical values10,11,23 and thus unreliable in structural determination. However, the bandgap calculated with the MIN basis set based on the DNP (equivalent to DZP) optimized silicene structure is only 20% larger than those with the DNP basis set (see Figure S2b, Supporting Information).

The linear dependence of Eg on E± is well explained in terms of a tight binding (TB) model calculation (see Supporting Information), which gives Eg = eE±A, and the result is shown as the dashed lines in Figure 3a. The band gaps of the TB model are several times larger than those of DFT because the screening effect is not taken into account in our TB model. Mulliken population analysis

displays a net charge transfer from one atom to the other in the primitive cells of silicene and germanene (shown in Figure 3b), and the amount of the polarized charge increases linearly with E±. Therefore screening effect exists and is enhanced with E±. According to the TB model, silicene has a smaller A and thus has a smaller Eg than germanene, while in the DFT calculation silicene has a larger Eg. Although the polarized charge in silicene is larger than that in germanene, it does not mean that silicene's screening is greater than germanene's, because Mulliken population analysis is rough and incapable of taking the charge's spatial distribution into account. In fact, bulk germanium has a larger dielectric constant (e = 16.0) and therefore more powerful screening effect than silicon (e = 11.9) does. In our self-consistent DFT calculation, the larger screening effect in germanium leads to a smaller band gap in germanene compared with silicene.

The variations of effective carrier masses of silicene and germanene along several directions in k-space under electric field are investigated by quadratic polynomial fitting of the conduction and valence bands (see Supporting Information). The effective masses of the conduction band bottom of silicene and germanene along the MK (meMK) and KT (meKr) are plotted in Figure 3c. The meMK values of silicene and germanene are larger than their respective meKr. All the four effective masses have an

approximately linear relationship with E^, and the linear dependence of the effective me on E± remains in other directions we checked. Such a linear relationship of me on E± is also well explained in terms of the TB model (dashed lines in Figure 3c).

The latter gives an isotropic effective electron mass (see Supporting Information): me = (2h2ExeA)/(3a2y2), where y1 is the nearest neighbors' coupling coefficient. The effective mass of the valence band top (mh) is almost the same as that of the respective me with a difference within 2% in DFT and is exactly the same in the TB model due to the symmetrical band structure around Ef in silicene and germanene. At E± = 0.4 V/A, effective masses in silicene (meKr = 0.015 m0, meMK = 0.033 m0, where m0 is the free electron mass) and germanene (meKr = 0.014 m0, meMK = 0.029 m0) monolayers are compared with those in electric field free bilayer graphene (meKr = 0.028 m0, mh«r = 0.029 m0, meMK = 0.012 m0, and mhMK = 0.015 m0).9 Mobility /I and effective carrier mass m* have a simple relation: I = eT/m*. In light of the fact that suspended graphene has a mobility of I ~ 200 000 cm2 1 s—1,1—4 the mobilities of suspended silicene and germanene under E± = 0.4 V/A are estimated to be on the order of 105 cm2 V—1 s—1, if the scattering time T is similar between graphene and silicene/germanene.

In light of the reactive nature of sp3 hybridized silicene, the dielectric

should be carefully chosen. Experimentally, graphene has been deposited on an inactive hexagonal boron nitride (h-BN) multilayer, and the mobility of graphene is elevated by 1 order of magnitude compared with an SiO2 substrate-supported sample due to the smooth surface of h-BN.26,27 It is suggested that preservation of a high mobility in a dual-gated graphene device may be achieved by fabricating an h-BN/graphene/h-BN stack using a two-transfer technique.26 Theoretical investigation of h-BN/graphene/h-BN sandwich structure shows that electrical field-induced bandgap opening in bilayer graphene is nearly unaffected by h-BN.28 Our simulation shows that silicene will spontaneously form covalent bonds with both Si and O atoms on the common SiO2 dielectric (Figure S3, Supporting Information). However, both silicene and h-BN are approximately intact when placed on or sandwiched between h-BN even under an electric field of up to 2 V/A. Total energy of silicene/h-BN system as a function of the distance between silicene and h-BN is provided in Figure S4, Supporting Information, with an equilibrium distance of 3.30 A between silicene and h-BN. Figure 4a shows the sandwich structure under zero electric field. The buckling of silicene placed on (Figure S5, Supporting Information) or sandwiched between (Figure 4b) h-BN is also slightly enhanced by E^. The bandgap of silicene sandwiched between h-BN is even larger by 50% than that of

freestanding silicene under the same EJ (see Figure 4c). Therefore, insertion of h-BN buffer layer between silicene and oxide substrate is strongly recommended in a silicene FET device to maintain the structural integrity and high carrier mobility. In the dualgated silicene FET, silicene should be sandwiched between h-BN buffer layers. Our simulation shows that even single layer h-BN is nearly flat on SiO2 surface (Figure S6, Supporting Information) (multilayer h-BN is more robust against buckling); therefore the structure of silicene sandwiched between h-BN buffer layer can be maintained when placed on SiO2 dielectric.

The model of a dual-gated silicene FET with SiO2 dielectric and h-BN buffer layer is shown in Figure 5 a. Different from a single-gated FET, a dual-gated device can control not only the doping level but also the vertical electric field applied to the monolayer. The top and bottom gate voltages are labeled by Vt and Vb, respectively. The distance between the two gates is d0 = 20 A in our model, and the thickness of the both top and bottom dielectric plus buffer regions is di = 7 A. To avoid an insulator-to- metal transition in few-layer h-BN caused by the Stark effect and to ensure the system can endure a strong electric field, the number of layers of buffer h-BN should be limited according to the DFT calculations.29,30 According to the DFT calculations, h-BN trilayer remains semiconducting under Ej = 0.829 or 1 V/A30 and can be used as buffer layer working under a strong

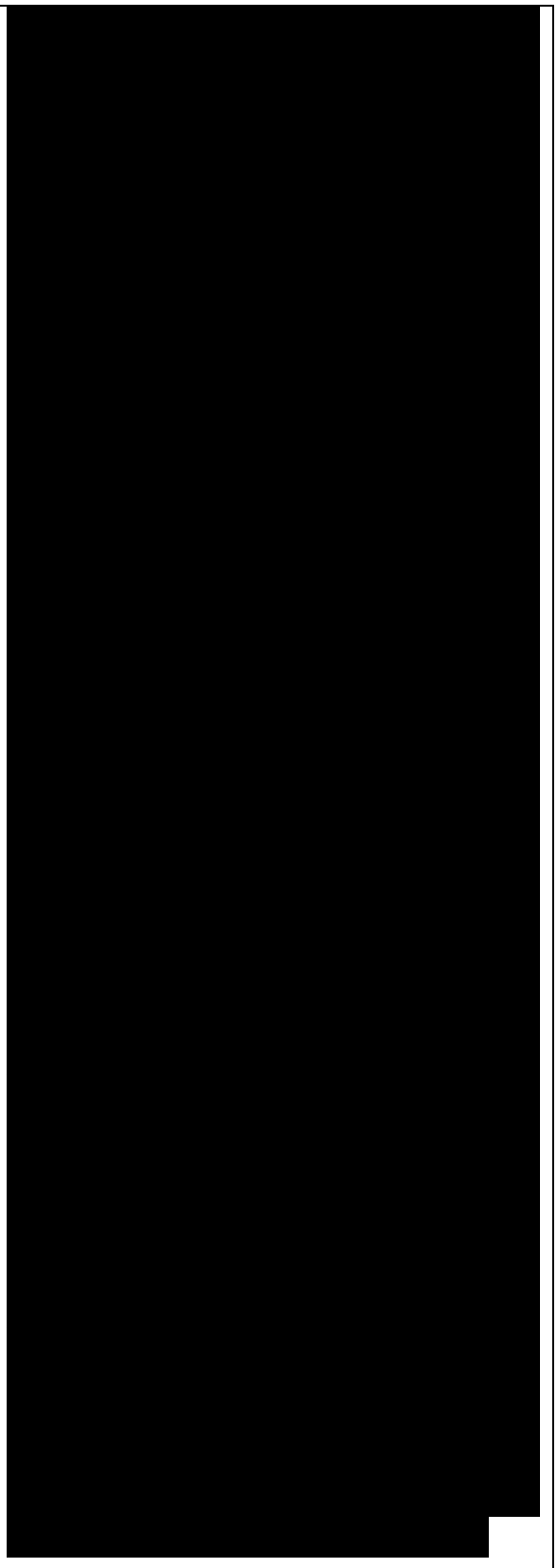
electric field up to 0.8-1 V/A, since h-BN trilayer probably can effectively prevent a tunneling between the gate and silicene. The dielectric constant of the dielectric and buffer regions is taken as e = 3.9, which models SiO2 and h-BN (e = 3-4). The vertical electric field applied to a silicene can be written as EJ = (Vt - Vb)/(d0 - 2di + 2di/e). The corresponding total gate voltage is Vg = Vt + Vb, reflecting the total doping level.

The transmission spectra of the device with a channel length of ^67 A under different Ej and Vg using an SZ basis set are displayed in Figure 5b, where the bias voltage is fixed at Vbias = 0.1V. As we know, the total conductance G(Ej, Vg) of an FET is proportional to the projected density of states (PDOS) of electrodes (denoted as Dl(Ej, Vg) for the left one and DR(E±> Vg) for the right one) and the channel cell (denoted as Dc(Ejl, Vg)):3^32

if the device is considered to be three resistors in series. Under Vbias = 0.1 V, the Dirac points of the source and drain in silicene FET move to ±0.05 eV, respectively, regardless of EJ and Vg.

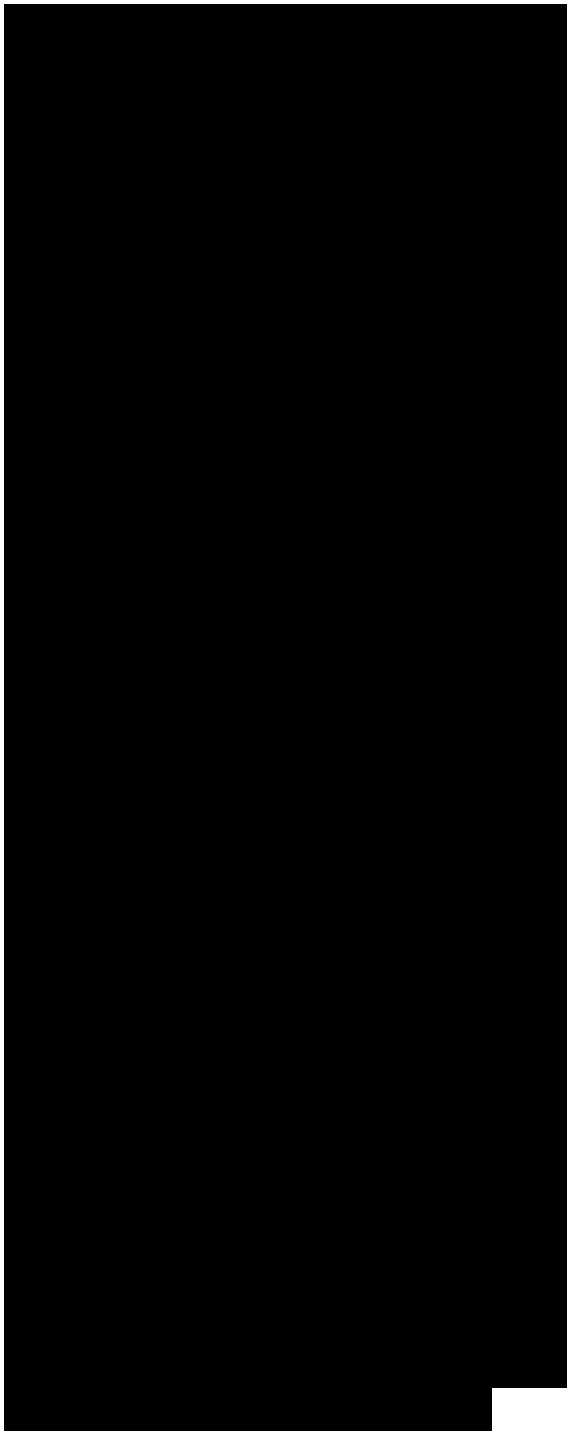
Under zero vertical electric field, there is a transmission “bulge” around Ef inside the bias window at Vg = -0.2 V for both the SZ (Figure 5b) and DZP (Figure S7, Supporting Information) basis sets. This is exactly as the case of graphene,32 in which the relatively large transmission coefficients inside the bias window (i.e., the “bulge”) lead to a relatively large current.

However, upon the application of EJ = 1 V/A on silicene, an obvious transport gap of about 0.14 eV is opened (Figure 5b) due to the occurrence of an about 0.12 eV pseudogap in DC(EJ, Vg) (Figure 5c) with an SZ basis set used, which apparently originates from the band gap of periodic silicene under the same EJ. The channel PDOS pseudogap and the transport gap can be shifted by Vg (Figure 5b, c and Figures S8 and S9, Supporting Information). Under Vg = 1V, both the two gaps are moved away from the bias window, resulting in the recovery of the bulge, and the device is turned from off- to on-state. Vg = -0.2 V is chosen to represent the off-state instead of Vg = 0 since the former case has smaller current, owing to the asymmetry of the transport gap around Ef. The difference in the off- and on-state is reflected from the transmission eigenchannel at Ef and at the (0, 1/3) point of k-space, as displayed in Figure 5d. The transmission eigenvalue of the off-state is 0.09, and the corresponding incoming wave function is apparently scattered and unable to reach to the other lead. On the contrary, the transmission eigenvalue of the on-state is 0.87, in which case the scattering is weak, and most of the incoming wave is able to reach to the other lead. The on/off current ratio under EJ =1V/Ais 4.2 with the SZ basis set at 300 K When a larger DZP basis set is used, a smaller pseudogap of about 0.1 eV in the transmission spectrum is opened under EJ = 1 V/A (Figure S7, Supporting Information), and the



on/off current ratio is reduced to 1.7. The current switch effects in vertically biased silicene are much weaker when compared with a traditional MOSFET, where the bandgap is more than 0.4 eV and the on/off ratio is 104-107.33 The first cause is the use of a rather short channel (^67 A), which gives rise to a larger leakage current in the off-state due to tunneling. Previous ab initio transport simulations34,35 have shown that on/off ratio increases apparently with the channel length for a graphene nanoribbon and carbon nanotube due to the reduced current leakage in the off-state (namely short channel effect). For examples, when the channel length of a graphene nanoribbon- based FET is increased from 17 to 68 A, the on/off ratio is raised by a factor of 104,34 and when the channel length of a function- alized single-walled carbon nanotube based FET is increased from 22 to 66 A, the on/off ratio is increased by a factor of 105.35 In our case, when the channel length of silicene is increased from 67Aby a factor of 1.5 at EJ = 1 V/A, the on/off ratio is increased to 7.4 (SZ) and 2.2 (DZP) (Figure S10, Supporting Information), respectively. When the channel length is further increased by a factor of 1.9 at EJ = 1 V/A, the on/off ratio is increased to 8.3 (SZ) and 2.6 (DZP). A larger on/off ratio is expected if the channel length is further increased and the device is further optimized.

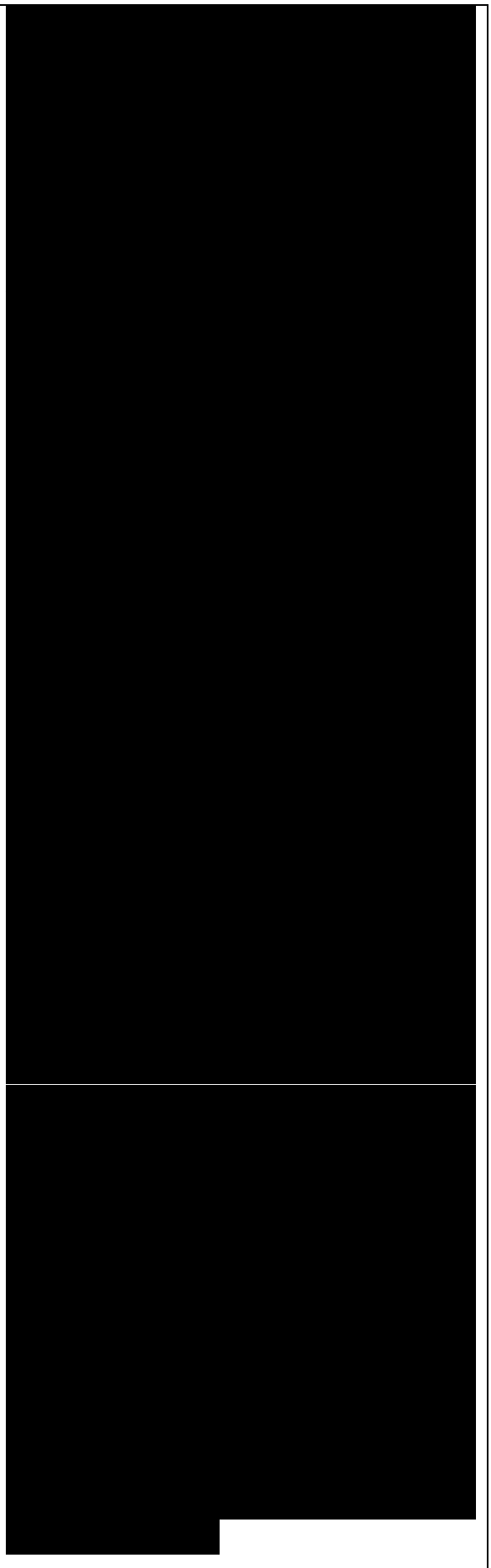
Second, it is well-known that the conventional DFT has a tendency to underestimate the bandgap a



semiconductor and that a quasiparticle correction (GW method) is required to obtain a reliable bandgap. Taking bulk Si as an example, the bandgap correction is increased by a factor of 150% upon quasiparticle correction. Such a bandgap correction is generally enhanced when dimensionality is reduced,24,36 and the bandgap correction in 2D silicene is expected to be greater (over 150%) than the correction in bulk silicon. The bandgap ofsilicene under EJ= 2 V/A is twice that under E J= 1 V/A and is chosen here as an approximation of the GWbandgap under EJ= 1 V/A. Compared the case with EJ= 1 V/A, the PDOS and transmission spectra are further depressed near Ef at EJ= 2 V/A, as shown in Figures S7 and S8, Supporting Information. The DFT on/off ratio of a 67 A channel FET under EJ= 2 V/A is 50 with an SZ basis set, and the on/off ratio under EJ= 1 V/A is thus estimated to be 50 upon GW correction. By sharp contrast, the current change ratio is only 1.07 (DZP) ~ 1.12 (SZ) for silicene without a vertical electric field. Hence, a current switching effect induced by perpendicular electric field is well established in our dual-gated silicene FET model.

Finally, we must point out that simply obtaining a large on/off ratio of silicene and graphene is not very difficult. For example, by cutting graphene into a nanoribbon, the on/off ratio can reach 106.37 However, one thing must be kept in mind that one of the most striking merits of silicene and graphene is their extraordinary high carrier

mobility, which is 1 -2 orders higher compared to a Si semiconductor and can lead to a quicker switching speed. It is a great challenge to simultaneously obtain high on/off ratio and keep ultrahigh carrier mobility in silicene and graphene, because the switching effect usually increases with the bandgap whereas the mobility usually decreases with the bandgap. The available methods to obtain a high on/offratio in graphene always lead to a drastic decrease in the carrier mobility by several orders of magnitude, totally losing the mobility advantage of graphene. If we want to maintain the extremely high carrier mobility of silicene and graphene, we have to compromise on the switching effect. Actually, as a feasible way to open a bandgap of bilayer graphene up to 0.25 eV7 without loss in carrier mobility, the measured room-temperature on/off ratio in a vertically biased bilayer graphene FET is only increased by a factor of 25 than that of the unbiased one.38 In our work, the enhancement factor of vertically biased silicene with respect to the unbiased one is 8 (when the SZ basis set and a 130 A long channel are used) to 50 (with possible GW correction and 67 A long channel). Such enhancements are encouraging because the opened band- gap of silicene under an electric field of 1 V/A is only half the maximum bandgap (0.25 eV) of bilayer graphene opened by an electric field, and the extremely high mobility of silicene (w ~ 104-105 cm2 V 1 s 1 in terms of our previous estimation of fl ~ 105cm2V 1s 1 at



Ej = 0.4 V/A and the relation of m* « Ej shown in Figure 3C and also derived in the Supporting Information) is maintained simultaneously. In summary, our ab initio calculations reveal one prominent advantage ofsilicene and germanene monolayers over a graphene monolayer. Namely, it is possible to open a bandgap in semi- metallic low-bulked silicene and germanene monolayers via an external vertical electric field, while it is impossible in a semi- metallic planar graphene monolayer. The bandgap and effective masses of both electrons and holes increase linearly with the electric field strength. An electrical field-induced transport gap is calculated in a simulated dual-gated silicene FET device, which enables us to switch the current of such a silicene-based device. Our work is expected to stimulate the experimental fabrication of FET out of pristine silicene and germanene monolayers.