A High Current Density Direct-Current Generator Based on a Moving van der Waals Schottky Diode

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Traditionally, Schottky diodes are used statically in the electronic information industry while dynamic or moving Schottky diode–based applications are rarely explored. Herein, a novel Schottky diode named “moving Schottky diode generator” is designed, which can convert mechanical energy into electrical energy by means of lateral movement between the graphene/metal film and semiconductor. The mechanism is based on the built-in electric field separation of the diffusing carriers in moving Schottky diode. A current-density output up of $40.0 \, \text{A} \, \text{m}^{-2}$ is achieved through minimizing the contact distance between metal and semiconductor, which is $100–1000$ times higher than former piezoelectric and triboelectric nanogenerators. The power density and power conversion efficiency of the heterostructure-based generator can reach $5.25 \, \text{W} \, \text{m}^{-2}$ and $20.8\%$, which can be further enhanced by Schottky junction interface design. Moreover, the graphene film/semiconductor moving Schottky diode–based generator behaves better flexibility and stability, which does not show obvious degradation after $10000$ times of running, indicating its great potential in the usage of portable energy source. This moving Schottky diode direct-current generator can light up a blue light-emitting diode and a flexible graphene wristband is demonstrated for wearable energy source.

Since the invention of Schottky diode at $1947$,[1] many important applications have been developed including high power, high speed electronic devices, etc.[2] However, the moving Schottky diode is rarely explored since all the applications are focused on the static structure. In $2006$, Wang and Song discovered that a rectified ZnO Schottky diode can output electricity due to the combination of piezoelectric and semiconductor properties of ZnO, which we called piezoelectric nanogenerator.[3] In $2012$, Wang and co-workers demonstrated triboelectric nanogenerator using the charging process in friction to convert mechanical energy into electric power for driving small electronics.[4] However, without rectifying circuit, the piezoelectric and triboelectric nanogenerator can only output alternating current and the output current density is quite small $(0.01–0.1 \, \text{A} \, \text{m}^{-2})$, which limits its widespread applications.[6]

Recently, the vertical movement between the metal and semiconducting polymer has been demonstrated to output intermittent current peaks with low current density $(2.7–62.4 \, \mu\text{A} \, \text{cm}^{-2})$, where the metal contacts with polymer periodically. On the other hand, the microscale direct current generator based on sliding between metal tip and semiconductor has been demonstrated,[8] where the mechanism was ascribed to the triboelectric effect. However, the mechanism of triboelectric effect is confusing,[9] as the fundamental physical mechanism of the charge transfer process during friction is not solved.[6,10]

Herein, we have demonstrated a macroscale direct-current generator through a moving van der Waals Schottky diode by dynamically moving graphene or metal film over Si or GaAs substrates. The mechanism of the moving Schottky diode generator is based on the built-in electric field separation of the diffusing carriers emitted by the appearance and disappearance of the depletion layer in moving Schottky diode. The working lifetime and flexibility can be properly improved by choosing graphene as the metal material, which is outstanding not only because of its high conductive but also the high mechanical physical properties.[11,12] Actually, static graphene/semiconductor van der Waals heterostructure-based solar cells,[13] self-driven photodetectors,[14] and water flow nanogenerator[15] have been proposed. Compared with metal, graphene film has the unique advantage of high flexibility and durability, which promises the graphene film/silicon moving Schottky diode generator working well after $10000$ runs back and forth. The persistent direct-current generating ability firmly demonstrates that the physical mechanism of the moving Schottky diode generator is not caused by the triboelectricity. Instead, we uniquely propose that the dynamic disappearance and establishment of Schottky junction during the movement between graphene/metal and semiconductors is the origin of the direct current output. The proposed mechanism is self-consistent and can well explain the systematic experiments presented herein. This moving Schottky diode direct-current generator can light up a blue light-emitting diode (LED) and a flexible graphene wristband is demonstrated for the first time. Under the guidance of the mechanism, we achieved a current-density output up of $\approx 40 \, \text{A} \, \text{m}^{-2}$ through minimizing the contact...
distance between metal and semiconductor by moving a metal tip on semiconductor surface. This direct-current generator has the potential of converting mechanical and vibrational energy into electricity and enables many promising applications.

As a representative moving Schottky diode generator, the 3D diagram and schematic structure of the moving graphene film/Si Schottky diode–based generator are illustrated in Figure 1a. The graphene or metal film was pressed to the semiconductor substrate compactly with a constant force when we move it on the semiconductor surface. When the graphene or metal film was dragged along the surface of the semiconductor substrate, a voltage or current output can be observed. As a representative system, the graphene film/Si heterostructure shows excellent rectification behavior with a low leakage current of ≈ 2 nA under a bias voltage of 1 V (the top inset of Figure 1a). The work function of N-type Si and P-type Si we used is approximate to its conduction band or valence band, i.e., 4.30 and 4.96 eV (the calculation is listed in the Supporting Information), respectively. The work function of graphene (≈ 4.6 eV) is different from that of Si,[12] thus a built-in electric field will form between the graphene film and the P-type/N-type Si substrate. For example, when the graphene film touches an N-type Si substrate by van der Waals force, electrons of the side of N-type Si will inject into graphene and an electron depletion region will form in the N-type Si substrate. The barrier height of graphene film/Si heterojunction can be extracted by fitting dark current density–voltage (J–V) curves, which can be written as follows:

\[
J = J_0 \left( \frac{qV}{N_F KT} \right) \exp \left( \frac{-q\Phi_{\text{barrier}}}{KT} \right)
\]

where \(K\) is the Boltzmann constant, \(T\) is the temperature, and \(N_F\) is the ideality factor. According to the thermionic-emission theory, \(J_0\) is the reverse saturation current density, which can be expressed by

\[
J_0 = A^* T^2 \exp \left( -\frac{q\Phi_{\text{barrier}}}{KT} \right)
\]

where \(A^*\) is the effective Richardson constant of n-Si, \(\Phi_{\text{barrier}}\) is the barrier height of the junction, and \(q\) is the quantity of electric charge. Based on Equations (1) and (2), the calculated \(N_F\) and \(\Phi_{\text{barrier}}\) of graphene/Si heterostructure are 15.2 and 0.718 eV, respectively (the calculation is listed in the Supporting Information). Primarily, the graphene film was dragged along the surface of the N-type Si at a dragging speed of 2 cm s\(^{-1}\) and a voltage output of 0.1 V has been observed, which increases as the dragging speed increases (Figure 1b), as well as the current. As the dragging speed increases up to 4 cm s\(^{-1}\), a voltage output of 0.18 V can be achieved. The voltage output can reach a maximum value of 0.22 V and remains stable when the dragging speed is as high as 6 cm s\(^{-1}\). Furthermore, the dependence of the output of the moving graphene film/Si Schottky diode under the force exerted on graphene is shown in Figure 1c and it is found that a force of 5 N is an optimal choice, where the diode has the best rectification characteristic (as shown in J–V curves and \(N_F\) of heterojunction under different force in Figure S1 in the Supporting Information). With the force increasing, the voltage and current output increase and then decrease with the change of the rectification characteristic of the graphene/Si heterojunction. As shown in Figure 1d, some other materials

Figure 1. Experimental designs and results of the moving heterostructure-based generator. a) Experimental design for converting mechanical energy into electrical energy by a moving Schottky diode. Inset at top shows the I–V curve of the graphene film/Si heterostructure-based generator with the contact area of 1 cm\(^2\). The voltage and current outputs of the graphene/N-type Si generator with b) different speeds and c) different forces applied to the heterojunction. The work area is 1 cm\(^2\). d) The voltage and e) current outputs of graphene, ITO, and Al/N-type Si generator with the work area of 1 cm\(^2\). f) The current output of the Al/N-type Si generator with different work areas.
such as indium tin oxide (ITO) and aluminum have been studied instead of the graphene film. The voltage output of the smooth aluminum film can reach the highest voltage up to 0.6 V at a dragging speed of 6 cm s\(^{-1}\), which is 3 times of the moving graphene film/Si Schottky diode–based generator. The work function of metallic aluminum is about 4.28 eV, which is smaller than Fermi energy of the Si substrate, so the generated voltage direction is opposite to the graphene film. The current output of different materials also increases as the dragging speed increases, which is up to 4 \(\mu\)A of the moving aluminum film/N-type Si Schottky diode when the dragging speed reaches 6 cm s\(^{-1}\) (Figure 1e). Besides, the current output also increases linearly as the area of the metal film increases, as shown in Figure 1f. The N-type GaAs substrate has also been chosen to measure the voltage and current outputs of the moving Schottky diode–based generator with different speeds and materials, whose results are listed in Figures S2 and S3 (Supporting Information). Some detailed results about the N-type Si substrate–based generator are also listed in Figure S4 (Supporting Information) for comparison. Normally, the Si substrate–based generator has a better performance compared with the GaAs substrate–based generator. Overall, a novel moving Schottky diode–based generator composed by a series of materials has been realized, demonstrating the repeatability and universality of the moving Schottky diode generator.

We propose that the dynamic appearance and disappearance of the depletion layer in the moving Schottky diode, which causes the separation of drifted electrons and holes, should be the origin of the electrical power generation. For the film/Si heterostructure system, the drift–diffusion equation and current can be described as follows:

\[
J_n = J_n^{\text{drift}} + J_n^{\text{diff}} = qn\mu_n \frac{\Delta U}{\Delta d} + qD_n \nabla n \tag{3}
\]

\[
J_p = J_p^{\text{drift}} + J_p^{\text{diff}} = qp\mu_p \frac{\Delta U}{\Delta d} - qD_p \nabla p \tag{4}
\]

where \(J_n, J_p, \mu_n, \mu_p, D_n,\) and \(D_p\) are the electron/hole current density, the electron/hole mobility, and the electron/hole diffusion coefficient in semiconductor, respectively. \(U\) is the potential, \(d\) is the distance of the built-in electric field, \(q\) is the elementary charge, and \(n\) and \(p\) are the position-dependent electron density and hole density in semiconductor, respectively. As schematically shown in Figure 2, there is a process of appearance and disappearance of the depletion layer when the metal/graphene films move along the silicon surface. When the metal/graphene film touches the Si substrate, the depletion layer will form at the interface of heterojunction immediately. Furthermore, the sliding of the film on the large area silicon surface will lead to the disappearance of the depletion layer in the rear end and the re-establishment of the depletion layer in the front end dynamically. We assume that the total contact area between the film and silicon surface stays unchanged. However, the dynamic appearance and disappearance of the depletion layer will break up the static carrier distribution and accelerate or bound back the electrons and holes which are diffusing across the depletion layer, depending the direction of the built-in field. This built-in electric field separation of the otherwise diffused electrons and holes emitted by the appearance and disappearance of the depletion layer in heterojunction causes the generation of current signal, which is defined as the moving Schottky diode generator. Thus,

**Figure 2.** The schematic diagram of the moving Schottky diode–based metal film/Si heterostructure generator with a) \(W_M < W_{n-Si}\), b) such as Al/N-type Si generator; c) \(W_M > W_{n-Si}\), d) such as Cu/N-type Si generator; e) \(W_M < W_{p-Si}\), f) such as Cu/P-type Si generator; g) \(W_M > W_{p-Si}\), h) such as Au/P-type Si generator. All the electrons and hole in the figure are accelerated or bound back by the built-in field at a subsequent time, depending on the Fermi level difference between metal and semiconductor.
the newly established depletion layer as well as the disappeared depletion layer emit the otherwise diffused electrons or holes maintaining the continuous voltage and current output. When we increase the moving speed, more diffused electrons can be bound back or accelerated by the built-in field, which increases the electricity output of the generator (Figure 1b). Besides, the direction of the voltage output is different because of the different work function of materials composing the heterojunction. When we use N-type Si substrate with the work function of 4.3 eV, the electrons in the metal film whose work function locates above N-type Si, such as Al, will transfer to the N-type Si while forming the built-in electric field. The moving Schottky diode–induced diffusing electrons will transfer to the metal film layer under the built-in electric field and form an electrical signal (Figure 2a,b). On the contrary, with the movement of heterojunction, electrons in the N-type Si substrate will transfer against the metal film whose work function locates below N-type Si (Figure 2c,d), such as Cu. Similarly, when we use the P-type Si substrate with the work function of 4.96 eV, the electrons of the metal film whose work function locates above P-type Si, such as Cu, will transfer to the P-type Si while forming the built-in electric field. The moving Schottky diode–induced diffusing holes in P-type Si will transfer against the metal film and form electrical signal (Figure 2e,f). On the contrary, with the movement of heterojunction, holes in the P-type Si substrate will transfer to the metal film whose work function locates below P-type Si under the built-in electric field (Figure 2g,h), such as Au. Some other cases about metal film/Si heterojunction-based generator are listed in Figure S5 (Supporting Information), which provide further evidence to support the above-mentioned mechanism.

As shown in the rectification characteristic of the moving graphene film/Si Schottky diode from −5 to 5 V (Figure 3a), the interface Schottky barrier varies when the graphene film/Si contact is under the friction process, which helps testifying the theory proposed above. The fluctuation of the I–V curve under friction condition compared with static condition is caused by the disappearance and generation of the depletion layer in the moving Schottky diode, which indicates the generation of the voltage output. Furthermore, as this process is caused by the separation of moving Schottky diode–induced diffusing electrons and holes in the Schottky diode, the generator can output continuous and direct electricity if we circularly move the film along the surface of the Si substrate. When the lateral movement between the film and semiconductor is rapid and continual, the induced voltage can be generated constantly. We have designed a generator system for continuously moving the graphene/metal film over the Si substrate (Figure S6, Supporting Information). Indeed, a direct voltage output of 0.6 V has been achieved based on the Al film/Si Schottky diode generator (Figure 3b).

Equations (3) and (4) can predict that the current density output changes with the contact distance between the metal/graphene and semiconductor substrate. As shown in Figure S7 (Supporting Information), silicon substrates with different surface silicon oxide are used and a decreased current is measured with the increase of the contact distance, attributing to the decrease of the built-in electric field at metal–insulator–semiconductor structure. For a large metal film putting on semiconductor, the microscopic fluctuation of the metal film will largely increase the contact distance between metal and semiconductor. Thus, we choose one metal Al tip with a small area of 0.1 mm² to testify the above-mentioned proposal. We measure the voltage and current outputs of the moving Al tip/Si Schottky diode generator as a function of the electrical load resistance as shown in Figure 3c. Accordingly, \( V_{oc} \) and \( J_{sc} \) can reach as high as 0.6 V and 40.0 A m⁻², which vary with the electrical load resistance. The power density is also changed with the electrical load \( R \) as shown in Figure 3d. Specifically, the peak power output \( P_{max} \) of 5.25 W m⁻² can be found around \( R = 200 \) kΩ, where the \( R \) value is close to the internal resistance \( r \) of the power generation unit. In contrast to the triboelectric effect, the otherwise diffused carriers emitted by the appearance and disappearance of the depletion layer only occur in the edge of film in the moving

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Figure 3. a) The rectification characteristic of the moving graphene film/Si Schottky diode from −5 to 5 V under 5 N force. b) The direct and continuous voltage outputs of the moving Al film/Si Schottky diode generator. c) Voltage and current outputs of the moving Al/Si Schottky diode generator as a function of the electrical load \( R \). The work area is 0.1 mm². d) Current density and power density output of the moving Al/Si Schottky diode generator as a function of the electrical load \( R \). e) The circuit diagram of directly and continuously charging capacitors without a rectifier bridge to light up the LED. f) Pictures taken from video to show the luminance of an LED powered by our heterojunction-based generator.
Schottky diode, so the current output is determined by the edge contact area and the contact distance, where a small contact distance leads to a largely enhanced current density output. The power conversion efficiency of the heterostructure based generator can reach 20.8% (the calculation is listed in the Supporting Information). It is worth mentioning that both of them can be further enhanced by the Schottky junction interface design.

In order to demonstrate the potential applications of this moving Schottky diode–based generator, we use capacitors to collect the electricity and then light up a light-emitting diode. Figure 3e shows the circuit diagram of directly and continuously charging capacitors without a rectifier bridge to light up the red LED. There are five generators and five capacitors used to storage enough power to provide the voltage output for an LED, which can work in 1.8–2.4 V driving voltage. Each of the generators can provide nearly 0.4 V voltage output, so five generators can light up the red LED here. The red LED has been successfully lightened after five 470 µF capacitors being charged for 15 min (Figure 3f). We can increase the output by optimizing the design of the generator structure in the future and then optimize this LED system. This direct-current generator has the potential of converting mechanical and vibrational energy into electricity and enables many promising applications.

However, the contact between the Al and Si substrate is very tough and thus induces the irreversible damage of the device, which limits its application. The working lifetime and flexibility can be properly improved by choosing graphene as the metal material. The illustration of the fabrication process of the graphene membrane is shown in Figure 4a–c. And SEM images of the graphene film have been supplemented to demonstrate its microstructure in horizontal and vertical directions (Figure S8, Supporting Information). It can be found that the graphene film fabricated is consisted of thousands of layers of graphene, which shows excellent flexibility. Compared with the performance decline of the moving Al/Si Schottky diode generator (Figure 4d), the graphene film can be stably used for the moving Schottky diode generator, which does not show obvious degradation after 10 000 times of running whereas the metal film degrades after 1000 times of running (Figure 4e). The flexibility characteristic of the graphene film ensures the smooth voltage output and limited substrate damage (Figure S9, Supporting Information). The rectification characteristic of the graphene film/Si heterostructure has also been measured, which shows limited damages after 10 000 times of running (Figure S10, Supporting Information). The calculated $N_{IF}$ and $\Phi_{barrier}$ of graphene/Si heterostructure after 10 000 times of running.
running is 21.2 and 0.652 eV, respectively, which show limited difference compared with initial values of 15.2 and 0.718 eV. After analyzing the influence of the force exerted on the graphene film/Si heterojunction, a force of 5 N was found to have the best rectification characteristic and maximum voltage output with limited damages to the Si substrate under continuous work condition (Figure S11, Supporting Information). Finally, a moving graphene/Si Schottky diode–based generator with great possibility for practical application is achieved, which can transfer the mechanical energy into direct current constantly. Figure 4f shows a flexible wristband based on the graphene/semiconductor generator, which is consisted of a 20 µm thickness of graphene film and a 2 µm thickness of GaAs film. And a continuous direct-current voltage output can be achieved with the lateral movement of two different films (Figure 4g), which shows excellent flexibility.

In this work, we have demonstrated a novel continuous direct-current generator based on the moving Schottky diode, which can convert mechanical energy into electrical energy by means of lateral movement between the graphene/metal film and the semiconductor. The mechanism highlights the built-in electric field separation of the otherwise diffused carriers emitted by the disappearance of the depletion layer in the moving Schottky diode. This proposed mechanism is self-consistent and can explain the systematic experiments presented herein. Lateral movement–induced voltage/current of the heterojunction is as high as 0.6 V and 40.0 A m–2, which is 100–1000 times higher than former nanogenerators. The power density and power conversion efficiency of the heterostructure-based generator is measured to be 5.25 W m–2 and 20.8%, which can be used to light a red LED after storage by capacitor. It is worth mentioning that the current density, power density and power conversion efficiency of this moving Schottky diode–based generator can be further enhanced by the Schottky junction interface design predicted by the proposed mechanism. This direct-current generator has the potential of converting mechanical, vibrational, and tidal energy into electricity and enables many promising applications.

**Graphene Thin Film Preparation:** The graphene membrane used in this work was synthesized with the few-layer graphene powder. The graphene powder used was synthesized by the oxidation–reduction method or the solvent stripping method. First, high purity and quality few-layers graphene powder was uniformly dispersed in a solvent such as DI water by the ultrasonic method. Then, the graphene membrane was obtained through tape casting on PET and dried in a hot plate at 80–90 °C. The few-layer graphene was suspended in DI water flatly and formed an ordered membrane layer by layer. Finally, the flat and continuous graphene membrane was exfoliated by a scraper after compaction and a large size of the flat graphene membrane is achieved.

**Devices Fabrication:** The graphene film was fabricated with a thickness of 20 µm. The Ohmic electrode on the graphene/metal film was formed by using silver epoxy and sealed using polydimethylsiloxane (PDMS) to avoid exposing to air. The thickness of other metal films including Cu, Al, and Au is 20 µm with the purity as high as 99.9%. The silver emulsion electrode was pasted on one side of the membrane in order to form good Ohmic contact, which was sealed using polydimethylsiloxane to avoid exposing to air. Meanwhile, single side polished N-type and P-type doped Si substrates were dipped into 10 wt% HF for 5 min to remove the native oxide layer, and then washed by deionized water. Ti/Au (5 nm/50 nm) contact was thermally evaporated on the unpolished back side of the Si substrate. The graphene/metal film was pressed adhesively to the Si substrate by hand or a holder, making sure a solid electrical contact between the graphene/metal film and the Si substrate can be established.

**Physical Characterization Methods:** The Raman spectrum of the graphene membrane was measured by Renishaw inVia Reflex with an excitation wavelength of 532 nm, and a laser with a power of ~1 mW was focused on the circle of radius 1 mm. The microstructure of the membrane was characterized with ZEISS microscopy. The current–voltage (I–V) data were recorded with the Keithley 2400 system and the Agilent B1500A system. The voltage and current responses with time were recorded in real time by a Keithley 2010 multimeter that was controlled by a LabView-based data acquisition system with a sampling rate of 25 s–1.

**Materials Characterization Analysis:** The Raman spectrum of the graphene film is shown in Figure S12 (Supporting Information), where the low intensity ratio between 2D and G peaks indicates that the graphene film used here is multilayer. The slightly visible D peak shows good quality of our graphene powder. The G peak of graphene used here blueshifts to 1583 cm–1 compared with 1580 cm–1 of the pristine graphene. Also, the 2D peak of graphene blueshifts to 2725 cm–1 compared with 2700 cm–1 of that of pristine graphene. The blueshift of G and 2D peaks indicates that the graphene film is a P-type doped.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

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