Tribovoltaic Effect on Metal–Semiconductor Interface for Direct-Current Low-Impedance Triboelectric Nanogenerators

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The triboelectric nanogenerator (TENG) is a new energy technology that is enabled by coupled contact electrification and electrostatic induction. The conventional TENGs are usually based on organic polymer insulator materials, which have the limitations and disadvantages of high impedance and alternating output current. Here, a tribovoltaic effect based metalsemiconductor direct-current triboelectric nanogenerator (MSDC-TENG) is reported. The tribovoltaic effect is facilitated by direct voltage and current by rubbing a metal/semiconductor on another semiconductor. The frictional energy released by the forming atomic bonds excites nonequilibrium carriers, which are directionally separated to form a current under the built-in electric field. The continuous average open-circuit voltage (10-20 mV), short-circuit directcurrent output (10–20 μ A), and low impedance characteristic (0.55–5 k Ω) of the MSDC-TENG can be observed during relative sliding of the metal and silicon. The working parameters are systematically studied for electric output and impedance characteristics. The results reveal that faster velocity, larger pressure, and smaller area can improve the maximum power density. The internal resistance is mainly determined by the velocity and the electrical resistance of semiconductor. This work not only expands the material candidates of TENGs from organic polymers to semiconductors, but also demonstrates a tribovoltaic effect based electric energy conversion mechanism.

power supply has become miniaturized, discretized, environmentally friendly, and sustainable, which poses new challenges for energy harvesting from ambient environment.^[1-4] As a new energy technology, triboelectric nanogenerators (TENGs) have the characteristics of light weight, small size, wide selection of materials, and high energy conversion efficiency, which can meet the energy demand of the information society.^[2,5,6] Compared with electromagnetic generators, piezoelectric generators, and electrostatic generators, TENGs have enormous advantages as a killer-level application to harvest the lowfrequency and small-amplitude abundant mechanical energy in the environment.^[7,8]

Based on the triboelectric effect and electrostatic induction effect, the traditional four modes of TENGs (contactseparation mode, lateral sliding mode, single-electrode mode, and freestandingtriboelectric-layer mode) can provide alternating pulses to the external circuit through the change of contact area or separation distance.^[9] However, conventional TENGs usually use organic polymer insu-

lation materials, and the charges generated by friction tends to

accumulate on the surface of the material, resulting in an alternating output.^[10–13] Recently, semiconductor materials began

to attract researchers' interest, and a series of work has made

great progress: the tribotunneling nanogenerator based on

1. Introduction

As an indispensable motive power for the advancement and development of human society, energy has always been a significant issue. With the advent of the Internet of Things (IoTs),

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DOI: 10.1002/aenm.201903713

sliding metal-insulator-semiconductor (MIS) structure,[14-17] the moving Schottky diode based on metal-semiconductor (MS) structure.^[18–20] the triboelectric cell based on PN junction structure.^[21-23] and other moving heterojunction nanogenerator.^[24] Thundat and Liu et al. realized an ultrahigh current density MIS nanogenerator due to quantum mechanical tunneling of the ultrathin natural oxide layer.^[14-16] Lin et al. designed a moving Schottky diode generator with high current density output which is based on the built-in electric field separation.^[18] Zhang and Xu et al. reported a direct-current triboelectric cell by sliding PN junction and indicated that its mechanism may be the formation of electron-hole pairs.^[22] It is true that these novel generators with continuous, high-density, and direct-current output characteristics have shown great interest and potential, but the power generation mechanisms of them remain to be extensively studied. Moreover, compared with the impedance of the electronic device or sensor $(\approx 100 \Omega)$,^[25–28] the internal impedance of these generators is still too large ($\approx M\Omega$).

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Herein, a metal-semiconductor direct-current triboelectric nanogenerator (MSDC-TENG) has been proposed. The mechanism of the MSDC-TENG can be attributed to the tribovoltaic effect^[22,29] of MS interface. The tribovoltaic effect is the creation of direct voltage and current by rubbing a metal/semiconductor on another semiconductor. The frictional energy released from forming of atomic bonds excites electron-hole pairs in semiconductor side and dynamic electron in metal side, which are directionally separated to form a current under the builtin electric field. The MSDC-TENG consists of a metal slider and an n-type doped silicon wafer coated with a back electrode. The continuous average voltage, direct-current output, and low internal impedance characteristic can be achieved by the relative sliding between the metal and silicon. Moreover, working parameters are systematically studied for the electric output and impedance characteristics of the MSDC-TENG. The results reveal that faster sliding velocity, larger load pressure, and smaller sliding block area can improve the maximum power density of the generator. The internal resistance of the MSDC-TENG is mainly determined by the sliding velocity and the resistance of the semiconductor. This work has not only expanded the material candidates of TENGs from organic polymers to semiconductors, but also demonstrated a tribovoltaic effect based electric energy conversion mechanism. This will promote the deep coupling of triboelectricity and semiconductor in the emerging field of tribotronics.

2. Result and Discussion

2.1. The Electric Output Characteristics of the MSDC-TENG and MS Interface Tribovoltaic Effect

To demonstrate the triboelectrification characteristics between metal and semiconductor, an n-type doped Si/stainless steel heterostructure MSDC-TENG is employed to measure the electric output characteristics under lateral sliding in **Figure 1**. The structure of the MSDC-TENG and 3D schematic illustration of the measurement setup are shown in Figure 1a. The metal slider reciprocates on the silicon wafer. The position and velocity of the slider are recorded in Figure 1b. The period of reciprocating motion is ≈ 0.12 s. The specific parameters of the experiment setup can be obtained in Table S1, Supporting Information. Under open circuit (OC) condition, the result shows that peak voltage is about 20 mV. The open circuit voltage (V_{oc}) has the same period as reciprocating motion (Δt). The generator has continuous voltage output during one motion period as shown in Figure 1c. With the decreasing of the load resistance from 1500 to 0 Ω , the average current significantly is increasing from 3.29 to 11.36 μ A. The short circuit current (I_{sc}) period is also Δt , as shown in Figure 1d. The impedance-matching curve can be obtained by the average current and power density at different resistances in Figure 1e. It can be clearly observed that the three working region behavior and the internal impedance of the generator is \approx 620 Ω . As summarized in Figure S1 and Table S2, Supporting Information, compared with the MSDC-TENG, conventional polymer TENGs have large internal impedance $(\approx M\Omega)$ and pulsed alternating current output.

It is well known that friction is a kind of energy dissipation process. There are eight dissipative mechanisms in literature research including: wear, molecular deformation, thermal effect, electronic effect, bonding, phonon effect, environmental and chemical effect, and structural effect.^[30] We believe that some of the mechanical energy can be absorbed by the electrons during relative sliding. Many phenomena have proved that, the electrons can obtain mechanical energy to jump to higher energy levels and even a exoelectron emission may form.^[31–33]

For the MS interface friction, when the work function of the metal is greater than that of the semiconductor $(W_m > W_s)$, the working principle and mechanism of MSDC-TENG is illustrated in Figure 2a. The energy band diagram of the MS junction can be illuminated in Figure 2b,c. In the initial status, the metal slider keeps still and a certain load pressure in good contact with the semiconductor. The electrons with higher Fermi levels will flow from the semiconductor to the metal side due to the Fermi level difference of the MS contact (Figure 2a, step 1). The flow of electrons causes the metal surface to be negatively charged, the semiconductor surface to be positively charged, and forms a built-in electric field. Consequently, the ideal MS contact band diagram of the equilibrium state is shown in Figure 2b. The energy band bends upward, and the built-in electric field is established in the extremely thin space charge region on the semiconductor side. However, when the metal slides on the surface of the semiconductor, there are two ways to generate moving carriers due to MS interface friction (see Figure 2c): i) In the space charge region of the semiconductor, the nonequilibrium carriers can be generated by the energy of friction. The friction-induced electron-hole pair can move along/against the direction of the built-in electric field. The electrons start a drift motion in the semiconductor while holes may also be driven to the MS interface under the built-in electric field. ii) On the metal and semiconductor surface state, the electrons obtain friction energy to jump to a higher energy level. The high energy electrons overcome the Schottky energy barrier flowing to the semiconductor side. The low energy electrons still have a certain probability of tunneling into the semiconductor side as long as the Schottky energy barrier is thin enough. The drift motion of electrons that cross the MS



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Figure 1. The electric output characteristics of the metal-semiconductor-based direct-current triboelectric nanogenerator (MSDC-TENG). a) The 3D schematic illustrations of the measurement setup and the external circuit. b) The relative position and velocity of the metal slider and the silicon wafer as a function of time. c) The oscillogram of open-circuit voltage. Inset: partial magnified view of the voltage. There is continuous voltage output during a sliding period (Δt). d) The current output with different load resistances (1500, 620, and 0 Ω). The above currents are calculated by the average of the selected 20 s current data. Inset: partially magnified view of the short-circuit current. e) Impedance-matching curve of the MSDC-TENG. Power density and average current as a function of load resistance.

interface occurs under the built-in electric field. As a result, the charge will flow through the MS interface to the external circuit (Figure 2a, step 2).

Therefore, the nonequilibrium carriers form a potential energy difference ($|q\Delta Vs|$) across the MS junction during the sliding process. This phenomenon is first attributed to the tribovoltaic effect by Wang,^[29] which is particularly similar to the photovoltaic effect by the frictional excitation rather than photoexcitation. This effect has multiple meanings. First, the released energy due to the newly formed atomic bond can be quickly taken by the electrons at metal side so that it jumps to an energy level significantly higher than Fermi level, followed by a flow to the semiconductor side as shown in Figure 2c. Second, during the friction process, the mechanical force causes the interface lattice to vibrate rigorously, resulting in an increase in the energy of the atomic system and the release of phonons. A part of the energy of the phonon is absorbed by the

electrons, which can excite electron-hole pairs at an MS junction if the released energy is high enough.

When the metal slider stops at the end of the semiconductor, at the same time, the electric field on the surface is reestablished and the charge no longer flows (Figure 2a, step 3). The reverse lateral sliding process (Figure 2a, step 4) is the same as in Figure 2a, step 2. When the metal slider remains stationary, the V_{oc} and the short circuit current I_{sc} are negligible as shown in Figure 2d, steps 1 and 3. Once the relative displacement is occurred between the metal and semiconductor, the V_{oc} and I_{sc} will be generated and remain stable while the velocity is constant (Figure 2d, steps 2 and 4). The DC characteristics of the TENG mainly depend on the built-in electric field. Thus, the current direction of the MSDC-TENG can be regulated via tailoring different MS friction pair. Based on the above theory, equivalent circuit diagram of the MSDC-TENG is drawn in Figure 2e. The generator can be simplified to three parts: a





Figure 2. The working principle of MSDC-TENG and tribovoltaic effect of metal–semiconductor interface ($W_m > W_s$). a) The working cycle of the MSDC-TENG. b) Energy band diagram of the MS junction in equilibrium states. c) Energy band diagram of the MS junction in sliding states. d) Schematics of the open-circuit voltage and short-circuit current of the MSDC-TENG. e) Equivalent circuit diagram of the MSDC-TENG.

friction-induced generation diode (V_S) and an internal resistance (R_I). The MSDC-TENG can provide continuous voltage (V_L) and direct-current output (I_L) for external load R_L .

2.2. Working Parameter Responses of the MSDC-TENG

In order to further explore the electrical output and impedance characteristics of the MSDC-TENG, the working parameter study is carried out, such as the sliding velocity and load pressure. The sliding velocity responses of the MSDC-TENG characteristics are first studied. In the first set of measurements, experiments are carried out using default setup, with the only variable of sliding velocity. From Figure S2a,b, Supporting Information, as the sliding velocity increases from 10 to 50 cm s⁻¹, the peak I_{sc} and V_{oc} output of the MSDC-TENG increase from 5 to 18 μ A and 2 to 20 mV, respectively. The average $V_{\rm oc}$ and $I_{\rm sc}$ versus sliding velocity curves exhibit linear variation and similar growth tendency as shown in Figure 3a. The increase of the sliding velocity not only increases the peak value of the $V_{\rm oc}$ and the $I_{\rm sc}$ in one working period but also shortens the working period of the generator. Therefore, the electric output performance of the generator is remarkably enhanced. The internal resistances and maximum power densities of the generator can be obtained by the impedancematching curves (see Figure S2c-g, Supporting Information) at different sliding velocities, as shown in Figure 3b. With the increase of the sliding velocity, the internal resistance of the MSDC-TENG decreases, while the maximum power density increases. A similar phenomenon can be found in the literature,^[9] and the optimal resistance is inversely proportional to the external excitation speed. Faster sliding velocity can excite the more electrons to achieve the higher maximum power

densities. Moreover, despite the sliding velocity of 10 cm s⁻¹, the internal resistance is only 3.3 k Ω , which has a low impedance advantage compared to the conventional TENGs.

We also measured the electrical output and impedance of the MSDC-TENG under different load pressures. The waveform diagrams of the I_{sc} and V_{oc} output are shown in Figure S3a,b, Supporting Information. When the load pressure rises from 2 to 18 N, the peak $I_{\rm sc}$ increases significantly, while the peak $V_{\rm oc}$ maintains constant at about 20 mV. Compared to 2 N load pressure, the average V_{oc} at 6 N load pressure increases sharply to 10 mV. However, the variation of the average I_{sc} is quite small in the range of 6–18 N. When the load pressure is 2 N, the MS contact is insufficient due to the unevenness of the microscopic surface, but good contact can be achieved under a large load pressure (6-18 N) in Figure 3c. It is noteworthy that the internal resistance decreases from 820 to 620 Ω when the load pressure is increased from 2 to 10 N, and then remains unchanged as shown in Figure 3d. The contact resistance has an impact on the internal resistance of the generator. As mentioned above, since the metal and the semiconductor are macroscopically in surface contact, and the two microscopic planes are rugged, the actual two surfaces are point contacts of many protrusions. As the load increases, the actual contact area of the two materials that are subject to friction increases. According to the law of resistance, we can conclude that the larger cross-sectional area can achieve the smaller resistance. As a result, the internal resistance of the generator decreases as the pressure increases. After the load pressure is increased to 10 N, the actual contact area of the metal is close to saturation, so that the internal resistance remains unchanged. Furthermore, the variation tendency of the maximum power density is similar with that of the I_{sc} . For the same reason, larger load pressure can increase the actual

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Figure 3. The dependence of the MSDC-TENG characteristics on the working parameters. a) The variation tendencies of average short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) with different velocities and their corresponding error bars. b) The internal resistance and maximum power density of the MSDC-TENG at different velocities. c) The similar curves as (a) except with different load pressures. d) The similar histogram as (b) except at different load pressures. e) The similar curves as (a) except with different sliding block areas. f) The similar histogram as (b) except with different sliding block areas. These data are derived from Figures S2a–e, S3a–e, and S4a–e, Supporting Information, respectively.

contact area of the metal and the semiconductor, resulting in improved power density.

The influence of different sliding block areas on the MSDC-TENG is also investigated. The I_{sc} and V_{oc} output of the generator were measured using the metal slider areas from 1 to 5 cm², respectively. As shown in Figure S4a,b, Supporting Information, an increase in the area of the slider enhances the output of the generator. It is assumed that the actual contact area of the MS is also increased with the augment of the slider area. The areas, which participate in the friction, become growing, so that more charges get excited. When the area changes five times than before, the average I_{sc} and V_{oc} only change about two times, as shown in Figure 3e. It shows that the electrical output performance of the generator is not a simple proportional relationship with the block area. When the two materials are in contact, the actual contact area between the two may only be 0.1% of the macroscopically observed contact area. The actual contact area on the microscopic surface during sliding does not depend entirely on the slider size. For the same reason, as the block area increases, the internal resistance of the MSDC-TENG first decreases and then remains unchanged, as shown in Figure 3f. The maximum power density decreases with the area increasing due to the growth rate of the power being lower than that of the area.

2.3. Resistivity and Doping Type Responses of the MSDC-TENG and DC Output Direction

In order to clarify the influence of materials on MSDC-TENG, silicon wafers of different resistivity and doping type were used. With different doping types and resistivities of the silicon





Figure 4. The dependence of the MSDC-TENG characteristics on the resistivity and doping type of silicon wafer. a) The variation tendencies of average I_{sc} and V_{oc} with different resistivities and types of silicon wafer and their corresponding error bars. b) The internal resistance of the MSDC-TENG at different resistivities and types of silicon wafer. These data are derived from Figure S5a–f, Supporting Information. c) The working cycle of the MSDC-TENG ($W_m < W_s$). d) Energy band diagram of the MS junction in equilibrium states. e) Energy band diagram of the MS junction in sliding states.

wafer, the average I_{sc} , V_{oc} output, and internal resistance of the generator are shown in **Figure 4**a,b, respectively. The friction between the two different types of silicon wafers and 304 stainless steel produces opposite direction of the current and voltage output as shown in Figure 4c. The work function of ordinary 304 stainless steel is about 4.34–4.47 eV.^[34,35] Through calculation,^[36] Table S3, Supporting Information, gives the work function of the silicon wafer used in our experiments according to the resistivity and doping type of silicon wafers. It can be found that the work functions of all the n-type silicon wafers are smaller than that of the stainless steel. On the contrary, the work functions of all the p-type silicon wafers are larger than that of the stainless steel.

According to the analysis of the working principle of the MSDC-TENG, we can deduce that the direction of the built-in electric field generated by the contact between stainless steel and n-type silicon is opposite to that between stainless and p-type silicon in Figure 4d. Therefore, the charges generated by the tribovoltaic effect and the nonequilibrium carriers move in the opposite direction under the built-in electric field as shown in Figure 4e. In this case, the electrons and holes are also generated possibly by the energy released from the forming of atomic bonds during friction at the p-type side. The strength of an atomic bond is about a few eV in energy, which is released when two atoms form a bond. For n- or p-type silicon wafers, there is a maximum average V_{oc} and I_{sc} on the curve. It can be assumed that when the work function of the silicon wafer is close to that of the stainless steel, on the one hand, the intensity of the built-in electric field is reduced and the drift speed of the nonequilibrium carriers is decreased. On the other hand, the Schottky barrier is lowered as well as there is more electric charge excited, across the Schottky barrier to form a drift current. It can be assumed that, when the work function of the

silicon wafer is close to that of the stainless steel, the intensity of the built-in electric field is reduced, and the drift speed of the nonequilibrium carriers is decreased. However, the reducing of the Schottky barrier causes more electric charge to be able to go across the Schottky barrier to form a drift current. These two effects are exactly opposite for the average I_{sc} and the V_{oc} , thus producing the curve is shown in Figure 4a. For the internal resistance of the MSDC-TENG, the resistivity of the silicon wafer shows a significant effect, as shown in Figure 4b. Regardless of the p-type or n-type doped silicon, the larger the resistivity, the larger the internal resistance of the generator. When the silicon resistivity is 20–40 Ω · cm, the internal resistance of the generator is 5 k Ω , which is eight times different from the internal resistance of the n-type doped silicon wafer resistivity of 0.002–0.004 Ω ·cm. This shows that the resistivity of the silicon wafer can effectively regulate the output internal resistance of the generator.

3. Conclusion

In this work, we propose a tribovoltaic effect based MSDC-TENG. The tribovoltaic effect is the creation of direct voltage and current by rubbing a metal/semiconductor on another semiconductor. The mechanism for DC is that frictional energy released from forming of atomic bonds excites electron-hole pairs in semiconductor side and dynamic electron in metal side, which are directionally separated under the built-in electric field. The MSDC-TENG can provide continuous DC output and low internal impedance, which can convert mechanical energy into electrical energy. The influence of working parameters is systematically studied, such as the sliding velocity, load pressure, sliding block area, and silicon wafer resistivity. The



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results reveal that faster sliding velocity, larger pressure, and smaller sliding block area can enhance the maximum power density of the generator. The internal resistance of the MSDC-TENG is mainly determined by the sliding velocity and the resistance of the semiconductor. By tailoring the MS material and structure of MSDC-TENG, it is possible to effectively control the electrical output and internal resistance of generator leading to optimized power output. This work has not only expanded the material candidates of TENGs, but also demonstrated a tribovoltaic effect based electric energy conversion mechanism, in which the friction action directly effects in the semiconductor interface. This will promote the deep coupling of triboelectricity and semiconductor in the emerging field of tribotronics.

4. Experimental Section

Fabrication of the MSDC-TENG: The Si wafers (single-side polishing) with different resistivity and doping type was purchased from Suzhou Research Materials Microtech Co., Ltd, which had the same thickness (500 μ m), size (4 in.), and crystal plane orientation [100]. After being ultrasonically cleaned by the alcohol and deionized water, aluminum thin film (100 nm) was coated on the matte side of Si wafer as bottom electrode via magnetron sputtering process. The upper cylindrical metal slider was made of 304 stainless steel with wire cutting, and the thickness was 6 mm. The MS interface of contact and sliding removed the surface natural oxide layer by mechanical methods.

Experiment Setup and Electrical Measurement: In all experiments, the silicon wafer was fixed and moved with the linear motor (Akribis SGL100). The metal slider was fixed to the bottom of the dynamometer probe and the load pressure was controlled by plane displacement platform. A 7½ digital multimeter (Keysight Truevolt 34470A) was applied to measure the current and voltage output. Data acquisition program was written by Python.

Data Process: The average current \overline{I} and voltage were obtained by calculating the mean of 20 s sampling data with ORIGIN Pro. Average power density \overline{P} was calculated as follows:

$$\overline{P} = \overline{I}^2 R \tag{1}$$

where *R* is the load resistance connected in the external circuit, \overline{I} is the calculated average current.

Supporting Information

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

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Nos. 51922023, 61874011), Beijing Natural Science Foundation (No. 4192070), and National Key Research and Development Program of China (2016YFA0202704). The authors also thank Yuanzhi Cao, Youchao Qi, Yaoyao Liu and Zhenyi Wang for the assistance in experiment and demonstration.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

direct-current, energy harvesting, low impedance, metal-semiconductors, triboelectric nanogenerators, tribovoltaic effect

Received: November 11, 2019 Revised: December 8, 2019 Published online:

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