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ELECTRIC GENERATORS BASED ON DYNAMIC SEMICONDUCTOR JUNCTIONS

XU RAN

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2020

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The contributions of the co-authors are as follows:

- Prof Q. Zhang provided the initial project direction and prepared the manuscript drafts.
- I co-designed the experiments with Prof Q. Zhang.
- I and Mr W. Cai performed all the laboratory work. I collected the data for semiconductor electrodes and Mr W. Cai collected results for metallic electrodes.
- I prepared the experimental section of the manuscript drafts with Mr W. Cai.

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The contributions of the co-authors are as follows:

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- Mr J. Y. Wang assisted in the preparation of electrodes.
- Mr D. Liu assisted in performing measurements in the vacuum chamber at Beijing Institute of Nanoenergy and Nanosystems Chinese Academy of Sciences.
- Prof. Z. L. Wang and Prof. J. Wang assisted in the interpretation of the data and discussion of the mechanism.

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Summary

Mechanical-to-electric energy generators are sustainable solutions in energy harvesting. There are mainly three categories: electromagnetic, piezoelectric and electrostatic. While they are proven to be capable of harvesting mechanical energy, some limitations are also identified. For example, electromagnetic generators are limited in device miniaturisation, while piezoelectric and electrostatic generators generate pure displacement current, thus are facing challenges in the power delivery efficiency as well as the constraint from RC time. Hence, it is promising to explore alternative mechanisms for electric generators that can enable more applications in energy harvesting.

In this dissertation, generators based on the dynamic semiconductor junctions with new mechanisms have been proposed and studied. By intermittently contacting and separating two semiconducting surfaces that possess different chemical potentials, both conduction current and displacement current have been generated, converting mechanical energy to electrical energy. Alternatively, by sliding two semiconducting electrodes against each other, direct current has been generated by coupling friction power and built-in electric field in the semiconductor junctions. The objectives of this thesis are to establish theoretical models for these generators, to develop protocol devices, and to identify the parameters affect the electrical energy generation.

The thesis is divided into three parts. In the first part, the study of triboelectric nanogenerators (TENGs) was focused. Three surface modification methods on the contact metal electrode have been performed to improve the electrical energy generation effectively, including using metal foams, introducing oxidization and

reduction reactions and roughen surface with sandpaper. Additionally, based on solid-liquid contact electrification and electrostatic induction, a water sensor for metal ion detection and pH value estimation has been developed.

In the second part of the thesis, a novel type of generator that generates both conduction current and displacement current by intermittently separating and contacting two oppositely doped semiconductor electrodes have been developed. The theoretical model for the generators was developed, and a comprehensive study with protocol devices was demonstrated and the response to RC time has been studied too.

In the last part of the thesis, a direct-current generator by sliding doped semiconducting/ metallic electrodes without changing contact area has been developed. The influences of friction power at the dynamic contact junction has been comprehensively investigated, and the theoretical model was established. Also, the influences of the electrode geometries and operating environments, such as air pressure, humidity and temperature, have been studied carefully.

For the two new types of electric generators based on dynamic junctions, they are capable to generate conduction current, which has potential in high frequency applications. Furthermore, as doped semiconductors or metals are used as electrodes, the generators can be easily integrated with other semiconductor devices applications.

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Abbreviations

TENG	Triboelectric nanogenerator
AC	Alternative current
DC	Direct current
XPS	X-ray photoelectron spectroscopy
MEMS	Microelectromechanical systems
PET	Polyethylene terephthalate
ITO	Indium tin oxide
PDMS	Polydimethylsiloxane
PVDF	Polyvinylidene fluoride
CNT	Carbon nanotubes
DI	Deionized
ZnO	Zinc oxide
MoS ₂	Molybdenum disulphide
FEP	Fluorinated ethylene propylene
PTFE	Polytetrafluoroethylene
LED	Light-emitting diode
NiO	Nickel oxide
LUMO	Lowest Unoccupied Molecular Orbit
SEM	Scanning electron microscope

Chapter 1   Introduction

1.1   Background and motivations

According to the statistical review of world energy from British Petroleum (BP) Energy released in June 2019 [1], the global primary energy consumption has grown fast at a rate of 2.9%, the highest among the ten years. Despite that among which 14.5% of the energy is provided through renewable power, traditional fossil fuels are still the primary source of energy generation, resulting in increased carbon emissions as well as environmental issues such as air quality and water pollution. It is crucial to find alternative ways of power generation with lower carbon emission and high sustainability. There are abundant energy sources in nature awaiting. Some well-known examples are solar energy, wind energy, nuclear energy, ocean tide energy, and so on. To convert generous mechanical energy to electrical energy is one of the attractive solutions. Typically, there are three categories of mechanical energy harvesters: electromagnetic, piezoelectric and electrostatic generators. To implement the energy harvesting system for each mechanism, extensive studies have been devoted, covering a wide range of fundamental science in energy transducer (to convert ambient energy to electrical energy), energy management (to control energy delivery) and energy storage (to optimise the energy usage) [2].

Electromagnetic generators

The electromagnetic generators have been developed since the early 1930s, based on the fundamental science as described by Faraday's law. When the magnetic flux through the enclosed area of a conducting coil varies, a potential difference can be induced, leading to a conduction current in the coil flowing in clockwise or counter-clockwise

directions [3]. Power is then delivered through electrical connections via the terminals of the coil to external loads R_L . Vibration and rotation are used to create relative motions between the coil and the magnetic field. In the need of device miniaturization, photolithography techniques are employed to fabricate micro-coils and various cantilever structures. For example, Wang et al. [4] fabricated a resonant structure where a polarised NdFeB permanent magnet resonated at the centre of a two-layer planar copper coil. They reported that an open-circuit voltage of 60 mV was generated at a resonance frequency of 121.25 Hz.

Piezoelectric generators

The piezoelectric generators can harvest mechanical energy with the use of piezoelectric materials. The piezoelectric materials are a group of special materials such that when a strain is applied, piezoelectric polarisation charges are induced along a particular orientation due to the breaking of central symmetry in the crystal structure, resulting in a potential difference at the two terminals [5]. As most of these piezoelectric materials are high in electric resistivity, the induced charges cannot flow through the material. Instead, the potential difference is balanced off by inducing electrons through external circuit, and discharge them off once the strain is released, which generates displacement current over the electrodes. For example, Yang et al. [6] reported a piezoelectric generator consisting of a single ZnO nanowire on a flexible substrate, such that by periodically bending and releasing the substrate with a strain of 0.05 – 0.1 %, an open-circuit voltage of 20–50 mV and a short-circuit current of 400–750 pA could be generated. Piezoelectric ceramic materials are widely used in piezoelectric generators [7]–[9], owing to their high dielectric property and piezoelectric voltage. The flexible materials like piezopolymers are also favourable for their improved deformability and durability. An interesting example was demonstrated by Li et al. [10] for wind energy

harvesting, where the piezoelectric materials were fabricated into dangling piezo-leaves, and with the vibration generated from wind blow, a peak output power density of 2 mW/cm³ from a single leaf was shown.

Electrostatic generators

The electrostatic generators are typically consisting of two electrodes separated with air gaps, dielectric materials or even vacuum. They can be used after being charged or with electrets that are embedded with surface potential V_s with dipole orientation or charge injection [11]. The potential difference changes with capacitance variation, such as relative motion, resulting in electrons flowing back and forth between the electrodes via electrostatic induction. Electrostatic generators are suitable for low-frequency mechanical energy harvesting, Tashiro et al. [12] developed an electrostatic generator harvesting the vibration of ventricular wall (1 to 2 Hz) to power up a cardiac pacemaker. A mean power of around 36 μ W was achieved. To achieve the miniaturisation of the generators, the techniques in micro-electromechanical systems (MEMS) are commonly used. The first MEMS-based electrostatic generator was developed using the in-plane overlap structure by Meninger et al. in MIT [13], the prototype device was able to convert ambient mechanical vibration to electrical energy, combining with IC optimisations, a power of 8.6 μ W was produced. Basset et al. [14] reported a MEMS electrostatic transducer on silicon, under a vibration at 250 Hz, an optimal power of 61 nW was converted.

Overall, all the three groups of generators generate AC, the net charge transferred within a complete cycle is zero. In other words, the amount of charges generated under the positive current is the same as that generated under the negative one. Furthermore, the electromagnetic generators generate conduction current only, where the current is due

to the flow of electrons in the coil. They are of low internal resistance and can be customised to accommodate for broad frequency range. However, the miniaturisation can limit their vibration amplitudes, which usually requests for complicated fabrication processes and results in lower output. The piezoelectric generators are useful in flexible energy harvesting devices, but their durability is challenged by the brittleness of the piezoelectric materials. Compared to electromagnetic generators, piezoelectric generators and electrostatic generators are more favourable in miniaturisation. However, they generate only displacement current via electrostatic induction, where the current is due to displacement of electrons in a time-varying electric field, and electrons move from one electrode the other through whole external load. Thus, their internal impedances are huge, which can be a main drawback in power delivery efficiency especially when high frequency charging and discharging are demanded.

Hence, it is necessary to explore alternative mechanisms for electric generators so that they can convert mechanical energy with a broad frequency range to electrical energy. Also, it is promising to have generators that can deliver energy to the loads without complicated conversions, so that a significant amount of energy loss can be prevented.

1.2 Objectives

This thesis will be divided into three parts. For the first part, a type of newly emerging generators - triboelectric nanogenerators (TENGs) will be focused on. The objective of this part is to improve the performance of the generators apart from existing complicated fabrication techniques. Also, an application as a water sensor, aiming to detect metal ion concentrations based on triboelectrification and electrostatic induction is to be developed.

In the second part, a novel type of generators by intermittently contacting and separating semiconductor electrodes is proposed. The objectives of this part are to develop the theoretical model for the generators, and to fabricate protocol devices.

In the third part, a direct-current generator based on dynamic semiconductor junctions is proposed. We aim to have a pioneering and comprehensive study on the mechanism of the generators. The influences of the materials, electrode properties, air pressure, humidity, temperature are to be investigated. The generators should harvest mechanical energy into electrical energy without being confined by RC time in the system. Moreover, the roles of the triboelectric effect in semiconductors electric generators should be addressed.

1.3 Major contributions of the thesis

The main contribution of this thesis is providing solutions with two new mechanisms for energy harvesting systems based on dynamic semiconductor contact junctions. Both mechanisms are excluded from the three groups of existing mechanical-to-electric energy generators. Specifically, in Chapter 5 and 6, a novel type of generators consisting of a pair of semiconducting or/and metallic electrodes with distinct chemical potential was first time proposed and studied. P-n junctions are elemental components in semiconductor devices, but we demonstrate the first-ever work to separate the junctions for mechanical energy harvesting. With intermittent contact-separate motions, both conduction current and displacement current were generated, and one-direction dominated current generation was realised. The theoretical model was developed, and the influences of frequency and RC time is analysed.

In Chapter 7, a direct-current generator by sliding doped semiconducting/metallic electrodes without changing contact area was developed, enabling continuous current

generation and constant voltage output unaffected by the RC time in the external circuit. The dependence on friction power at the dynamic contact junction was comprehensively investigated, and the theoretical model was the first time established, pioneering a new mechanism for mechanical-to-electric energy generator. Since doped semiconductors or metals are used as electrodes, the devices can be easily integrated with other semiconductor devices and IC chips to function as a power source or mechanical sensing. Also, as this generator converts friction power into electric signals instantaneously, it provides a new perspective in understanding triboelectric effects within dynamic semiconductor junctions.

Besides above, in Chapter 3, three surface modification methods including pressed metal foams, sandpaper polish, oxidisation and reduction processes were proposed to improve the performance of triboelectric generators, providing alternative engineering solutions for output enhancement apart from existing complicated and costly fabrication processes.

1.4 Organization of the thesis

This thesis presents the systematic study of new mechanisms for mechanical to electrical energy conversion. With identifying the limitations of existing generators, two new types of generators that generating currents through dynamic semiconductor junctions are proposed. The theoretical models are developed and investigated in coordination with comprehensive experimental results.

In Chapter 1, a brief introduction of the urgent demand for alternative energy sources and some commonly used mechanical to electrical energy converters are reviewed, the limitations of the present prevailing methods are identified. This chapter includes the

motivations and the main objectives of this thesis and summarises the major contributions of this PhD project.

A literature review is given in Chapter 2. It provides the background knowledge of friction in different groups of materials and some important models for the common tribology behaviours. Next, the triboelectric effect is reviewed, including a summary of existing mechanisms for charge transfer and some common factors that influence the triboelectrification phenomena. It is followed by an introduction of the triboelectric generators (TEGs), including the working principles of TEGs and some major applications. Lastly, basic theories for the p-n junction in semiconductors are introduced.

In Chapter 3, a water sensor for metal ion and pH level detection based on solid-liquid electrification and electrostatic induction is presented. The mechanism and performance are discussed there.

Chapter 4 focuses on the fundamental study of TEGs, and it presents three surface modification methods to enhance the performance of TEGs. The influences of contacting force, operation frequency and load resistance were studied, and the drawbacks of TEGs will be highlighted.

Chapter 5 introduces a novel type of generator that generates one-direction dominated current by intermittently contacting and separating two semiconducting/metallic electrodes. The theoretical model for this generator is proposed, and performance from some protocol devices are demonstrated, and the influences of operation frequency and load resistance are discussed.

Chapter 6 introduces another innovative mechanical to electrical energy converter, called triboelectric cell. It generates direct current by sliding two semiconducting and/or

metallic electrodes against each other. The generators are studied via sliding speeds, electrode geometry, humidity, air pressure and temperature. A theoretical model is illustrated.

Lastly, Chapter 7 summarises the main results obtained in the thesis. Also, it recommends opportunities for future researches and suggests some research directions based on the contributions in this thesis.

Chapter 2   Review of Theory and Previous works

2.1   Friction

When a solid surface is examined in the micro/nanometre scales, it is uneven and contains a high density of asperities. Hence, when any two surfaces are brought together, only isolated points are in contact, this is called asperity contacts. These points deform under stress, responsible for all the contact interactions between the two surfaces. When the two surfaces move against each other via either rolling or sliding, there is always a friction force opposes the motion. Friction exists everywhere, and its magnitude varies for different materials and environments following The Laws of Friction [15], which states that:

- 1) the friction force is proportional to the normal force;
- 2) it is independent of the apparent contact area;
- 3) it is independent of the sliding velocity.

While the first two laws are well established, the last one is valid only for certain conditions, excluding the transition processes between static friction and kinetic friction or very high sliding speeds that are faster than tens of meters per second for metals. Due to ubiquitous presence of friction, it is essential to study the impacts of friction on mechanical energy to electrical energy conversion.

2.1.1   Origins of friction

The pioneer models for friction were proposed between the 1930s to 1970s, where it was believed that friction is caused by the mechanical interactions between the asperities [16]. The research for origins of friction has been remaining active till today. With modern techniques, the understanding of friction has been enabled at the atomic scale.

In the classic model of sliding friction [17], it is believed that the adhesion force and deformation force at the asperity contacts are the major components in friction.

The adhesion force is associated with the distortion of interfacial bonds, and it arises from the attractive force when the asperities are sufficiently close. In the case where the adhesion force is stronger than the internal cohesive strength of the materials, detach of material can be observed at the atomic scale [18]. The contribution of adhesion for the coefficient of friction μ_{adh} is estimated via $\mu_{adh} = \frac{F_{adh}}{W} \approx \frac{s}{H}$ [19], where F_{adh} is the adhesion force, W is the normal load, s is the shear strength and H is the indentation hardness of the softer material. The magnitude of μ_{adh} is clearly affected by the stiffness and the ductility of the asperities.

The deformation force is the other main component in friction force, especially for contacts where a hard material extends to a softer material. The deformation force is investigated with the model where the asperities are idealised as individual rigid conical shape with semi-angle α , and the coefficient of friction due to deformation force μ_{def} is usually estimated as $\mu_{def} = \cot \alpha$ [19]. However, for the friction between two hard surfaces, the deformation term is usually negligible comparing to that of the adhesion.

Besides the classical model, modern views suggest that dissipative processes also contribute to friction. For example, the energy consumption under the generation of phonons [20]. As the atoms in a crystalline solid are not rigidly bonded, when one surface slides over the other, the atoms near the surfaces can vibrate around their equilibrium states. This vibration generates elastic waves, which propagate away from the contact and dissipate energy.

2.1.2 Dominating factors in friction

The coefficient of friction μ varies within a wide range depended on the type of materials and experimental conditions [21], [22]. The adhesion and deformation forces contribute to friction under different mechanisms, resulting in distinct tribology properties.

Metals

The friction happens near a metallic surface is affected by multiple factors, such as the chemical and structural changes that occur at and near the surfaces when sliding in different environments. Studies often reported that the friction coefficients and wear rates in vacuum are found to be higher than those in air [23]–[26]. A commonly agreed explanation is that the oxide layer that formed on the surface due to the adsorption of gases in the air gradually forms a tribo-film during sliding, protecting metal surfaces from contacting, resulting in weakened shear stress and hence a smaller wear rate, and lower friction coefficient. For example Huang et al. [23] reported variation of friction when slide a Cu-MoS₂-graphite-WS₂ composite with Cu-Ag alloy in vacuum and in air, such that during steady state of sliding, the friction coefficient for sliding in vacuum was nearly 30% larger than that in air.

Temperature is another important factor that affects friction. The wear rate often increases when temperature is higher, which can be explained with the transfer of less tightly bound tribo-film. Also, a short-time interval high temperature gradient may result in unequal thermal expansion, the resultant mechanical stress lead to cracks of the tribo-film, contributing to the wear rate[23], [24]. In addition, with increasing temperature, chemical reactions at the surface may be involved, and the mechanical properties of the materials can be altered too.

Ceramic materials

Owing to the different interatomic forces, the friction in ceramic materials is lower than in metals. Similar to in metals, the friction between the ceramic surfaces can be affected by the chemical reactions at the interface, which is a complex consequence under the atmospheric composition, temperature, loads, sliding speed.

The friction can increase with the presence of fractures in ceramics, especially when sliding a hard pin or a sharp edge on a flat surface, which introduces additional energy dissipation and may even cause wear of materials. However, materials with lamellar structures, such as graphite and molybdenum disulphide (MoS_2), exhibit low friction generally [23], [27]–[32]. Owing to the layered structure, the covalent bonds between the atoms within the same layer are severely stronger than the interplanar bonding, result in low resistance to shear deformation and thus small values of μ_{adh} .

Polymers

Due to the viscoelastic property in polymers, the mechanisms of friction generation are fundamentally different from that in metals and ceramics [33]–[36]. As the strain can flow progressively around the asperity junction in polymers, each element experiences a deformation cycle while the strain moves, resulting in energy dissipation. Also, since the bonding within polymers is weaker than that in metals, the adhesion is more prominent, such that material transfer can happen easily when a polymer slides on hard surfaces.

2.1.3 Common friction behaviours

As discussed above, when two surfaces slide against each other, the friction is generated from the adhesion and deformation forces due to the asperity interaction. For surfaces with different asperity mass and stiffness, topology characteristics and local adhesion coefficients, the friction behaviours vary.

The Generalised Maxwell-slip friction model is used to simulate the friction behaviours, in which all the asperities on a surface are represented with N elementary systems. For each system, there is a block slide on a flat surface under the force of a linear spring, as shown in Figure 2-1 [21]–[23]. Initially, there is zero deflection at the junction, and when the force is very small, all asperities would be stuck. When the force is gradually increased, such that the force exerted on the i^{th} element reaches the threshold, element i slips. The whole system sticks until all the N elementary blocks slip, and the force required to initiate the slide motion is called breakaway force. After reaching the breakaway force, the system slides and meanwhile the asperity contacts are continuously being formed and broken, exhibiting a stick-slip behaviour.

Figure 2-1 The Maxwell-slip friction model using N elementary blocks [37]

The stick-slip behaviour can be simulated and experimentally visualised with the simple setup shown in Figure 2-2(a), where a block is pulled through a spring moving at constant speed v_0 . The position and velocity of the block as a function of time is shown in Figure 2-2(b). The block starts to slip when the force from the spring equals to the breakaway force; once it slips, the kinetic friction force decreases, resulting in a net pull from the spring and accelerates the block to move at a velocity faster than v_0 , shortening

the spring; the force applied on the block herein decreases, which subsequently decelerates the block until it sticks again. This stick-slip behaviour is commonly observed, the transition processes are complex and depend on many factors including the asperity mass properties and stiffness, as well as the relative velocity and acceleration.

Figure 2-2 Stick-slip behaviour. (a) Schematic of setup for studying the stick-slip behaviour. (b) Simulation results of the demand position (diagonal dot line) and demand velocity (horizontal dot line), and the real position of the block (full line) and the real velocity (dashed line) as a function of time. [37]

2.2 Theory of triboelectric effect

Triboelectric effect, or contact electrification, has been known for over 2500 years, existing everywhere in everyone's daily life, yet remains debatable over most fundamental questions. The scientific progress towards the basic principles of triboelectric effect is particularly slow. While it appears to be simple, to study the physics behind is rather complicated. For example, the defects or contaminations on a surface can cause significant effects and even dominate the charging behaviour, causing experiments are hardly reproducible. As triboelectric effect is a non-equilibrium phenomenon, it is necessary but challenging to investigate both charge transfer (< 1 ns) and bulk motion (~ 1 s) in theory contemporarily in a wide range of time scales [38].

This section summarises the deterministic theories and mechanisms about the triboelectric effect at current.

2.2.1 General parameters in evaluation of triboelectric effect

There are some general models to accurately evaluate triboelectric effect, i.e., charge injection depth and surface charge density. The triboelectric effect results in charge transfer and charge retain at the interface. The charges will be effective to a certain depth on each surface, and this depth is called charge injection depth λ [39]. To keep the additional charges, the surface must acquire capacitance characteristics. Depending on the material intrinsic, the equivalent capacitance C resulted from the charge with a thickness of λ can be simplified as $C = \frac{\epsilon S}{4\pi k \lambda}$, where S is the area size of dielectrics, ϵ the dielectric constant and k the electrostatic constant of the material [40]. Another important parameter is surface charge density σ , which measures the final charging effect for both surfaces and is usually taken to evaluate the efficiency in some triboelectric devices [40]. However, the total amount of charges driven from triboelectric effect can be much larger than the final charge, mostly due to the charge backflow during the friction motion at the interface, and the friction energy dissipation as triboluminescence [41].

2.2.2 Mechanisms of charge transfer

Despite the well-known phenomena of triboelectric effect, there is still a big debate over the type of species that has been transferred during the triboelectrification. Different theories have proposed electrons, ions and even nanoscopic materials.

Electron transfer

When considering electrons to be responsible for charge transfer, the work function (the energy required to release an electron) of materials (metals and semiconductors) is an

essential factor. It is commonly accepted and proved that when two metals or semiconductors are in contact, electrons are transferred from the material with lower work function to the one higher [42]. Based on this principle, Wang et al. [43] proposed the electron-cloud-potential-well model as shown in Figure 2-3(a). Initially, when two atoms from the two materials are separated, electrons are confined within their individual electron wells; with further shortening the distance and eventually move into the repulsive region, the two electron wells start to overlap, which allows the electrons with a higher chemical potential transfer to the lower side until they two reach equilibrium. After being separated again, the transferred electrons remain in the material as electrostatic charges. This theory is supported by quantum mechanical calculation that the strong stress from the overlap of electron clouds causes the delocalization of electron wave functions and hence drives electron transfer [44].

However, some studies believe it is trivial for electron transfer to happen in insulators simply because of the large gap between the valence band and conduction band, significant energy is required. Several papers pointed out that on non-ideal surfaces there are defects or surface states that can trap electrons in intermediate states within the bandgap and ease electron transfer process [45], and existence of those states was confirmed via some phosphorescence and thermoluminescence experiments reported previously [42], [46]. Nevertheless, more recent studies showed that the actual amount of charge developed is far beyond the amount of electrons that those states can possess [47].

Another model is the lattice vibration model which is based on the fact that triboelectric phenomenon is an energy-driving process, such that heat will be introduced via friction, which causes lattice vibration and generates phonons, and electrons are released to lower down the potential difference (Figure 2-3(b)) [48].

Figure 2-3 (a) The electron-cloud-potential-well model for triboelectric effect for two atoms before contacting, in contacting and after contacting [43]; (b) the lattice vibration model for triboelectric effect explanation [48].

Ion transfer

While electron transfer is plausible for triboelectric effect between metals and semiconductors, it is debatable for insulators. Especially noted that for neutral organic molecules, electron transfer is exclusive for conditions where the donor orbitals and the acceptor orbitals are well-matched. Also, the functional groups in most polymers do not usually appear to donate or accept electrons, and their ability of contact electrification is not affected by doping with electron-rich molecules [49], [50].

Based on the experimental observation that the contact electrification for insulators appertains to their acidity or basicity rather than bulk electronic preparties, the mechanism of proton-transfer was developed, which is an evident example of ion transfer [51]. Furthermore, as shown in Figure 2-4 [52], several groups observed the Lewis acidity and/or basicity of an insulating surface are correlated with its contact electrification behaviour [52], [53], whereas the oxidation-reduction (electron transfer) properties are not related [49], supporting the mechanism of ion transfer.

Figure 2-4 Correlation between the ordering of materials in the triboelectric series established experimentally and Lewis basicity/acidity [52].

Ion transfer between surfaces was further confirmed by modifying the binding strengths of ions. Reported by a few works [50], [54]–[56] that by modifying a surface to have a stronger binding with ions of one polarity while weaker to ions of the opposite polarity, after the modified surface contacted with a second surface, the weakly bound ions were transferred to the second surface while the strongly bound ones remained, leaving the surface possessing a net charge from the strongly bound ions.

As for materials without mobile ions, it was proposed that the absorption of water from the environment can give rise to triboelectric effect, where the OH^- and H^+ are responsible for charge transfer and the polarity of the triboelectric charges is decided by the binding strength of OH^- [50]. Experimental results supporting the charge transfer with water layer have been reported. For example, a neutral surface could get charged through varying the relative humidity, implying the ion exchange between water layer and environment [57]. Also, the magnitudes of electrostatic charges decreased with decreasing the pressure, which is potentially due to desorption of ions [58], [59]; lastly, the rate of electrification was observed to be affected by the hydrophobicity of the surface, suggesting the necessity of water layer presented [60].

Material transfer

As discussed in Section 2.1, when two surfaces are in contact, it is the asperities bear the pressure. Hence, the local strain increases and meanwhile results in higher local potential energy, as shown in Figure 2-5(a). Since materials tend to possess the lowest energy, they will begin to shift to the nearest minimum and establish a new energy-stable status [61], as shown in Figure 2-5(b), which is corresponding to the material transfer. Due to the breakage of original bonds, the transferred materials are likely to carry charges and result in triboelectrification. Baytekin et al. [62] studied the triboelectric effect between polymers with characterisation from x-ray photoelectron spectroscopy (XPS) and presented clear evidence of material transfer. Piperno et al. [63] also confirmed the material transfer using XPS and further proposed that the contact electrification is not only resulted from material change but also due to the change in ion binding strength.

Figure 2-5 (a) The potential energy variation and (b) the schematics of material transfer under the strain due to deformation [61].

In conclusion, while it is well accepted that electron transfer dominates for metal and semiconductor triboelectric effect, the charge transfer with insulators is never a single

mechanism, under different situations, more than one charge transfer mechanisms could be involved. There is still a big field awaiting further study.

2.2.3 Triboelectric series

Based on the result of triboelectrification of a material, the empirical triboelectric series were summarised to predict the direction of charge transfer among a wide range of materials, as shown in Figure 2-6(a) [38]. When two materials are contacted, the one more towards the (+) end of the table will be positively charged while the one more towards the (-) will be negatively charged. This table simplifies the analysis of the triboelectrification. However, interesting contradictory experiments were reported, such as the cyclic triboelectric series and the triboelectrification of identical materials, suggesting the complex factors in triboelectric effect.

Figure 2-6 (a) Example of a triboelectric series [38]; (b) Example of a cyclic triboelectric series [64].

Cyclic triboelectric series

One example in cyclic triboelectric series is shown in Figure 2-6(b) where the relationship of the materials cannot be ranged linearly, suggesting the ordering of the materials involves a combination of other physical properties, charge media and

electrification mechanisms [50]. However, Zhang et al. [52] had recently reported the linear ordering with these same materials, claiming that the Lewis basicity/acidity should be the only factor that affects the electrification in polymers.

Triboelectrification of identical materials

When two surfaces from the same material are contacted, the charge transfer is expected to be negligible. However, reproducible charge transfer was observed in many experiments [65]–[70]. Several mechanisms have been developed to understand the driving force for this charge transfer. Asymmetric contact was proposed to be one of the causes of charge transfer [68]. During the process when a surface with a smaller area is rubbed over another surface with a larger area, the charged species would transfer between non-equilibrium surface states. Initially, the probabilities for the charge transfer are identical for both surfaces; but when the smaller surface moves forward, its contacted region is in contact with a new region of the larger surface, where the two surfaces are now possessing asymmetric surface states, resulting in the accumulation of the charged species on the smaller surface. Also, calculated from the statistical variation expectation theory, the probability of directional charge transfer in symmetric contacts was shown to be proportional to the square root of the surface area [67], explaining the phenomenon mathematically. Moreover, the existence of external electric fields can polarise a material, which breaks the symmetry, resulting in charge transfer [71].

2.2.4 Factors that influence triboelectric effect

Along with the research on the triboelectric series, the results were not always reproducible, minor variation in material composition, environment or measuring equipment can lead to a different ordering. Some controllable factors are mainly from the surface properties and the environment influences. The geometry and surface roughness are believed to be vital for triboelectric effect as the local strain may trigger

different surface potential energy minimum and hence exhibit altered triboelectric behaviour [61]. Particle size dependence has been observed in many experiments where the smaller particles tend to be negatively charged while larger ones being positively charged. The reason behind is still unclear [38]. Humidity is another essential factor in triboelectric effects in a very sophisticated manner. While it is generally accepted that humidity increases the conductivity over a surface and hence reduces the electrostatic charging effect, some studies had observed the increased magnitude of charges when humidity is increased within a certain range [72]. It was proposed that the water molecules form a better connection when the surfaces are contacted and hence assist in charge transfer.

The amount of charge density that a surface can hold is limited. One important restraint is the dielectric breakdown of air, where the surface charges are to be conducted through the air when the potential difference of two surfaces is sufficiently high. Typically, according to Paschen's Law [73], the threshold electric field in air is 30 kV/m. Other limitations can be due to the electric field built up from the transferred charges repels further charging [74]. Also, the charge on a surface is hardly uniform, the net charge behaviour usually only indicates an average while local charge density can be much higher.

2.3 Triboelectric nanogenerators

The triboelectric effect is often considered as an adverse effect especially in the industry given that the electric discharge between two oppositely charged objects may lead to ignition, dust explosions, electronic damage, dielectric breakdown. When the charged objects are separated with a small distance, the triboelectric surfaces with the electrostatic charges accumulated is analogue to a capacitive energy device, based on

which, early electrostatic generators such as Van de Graaff generator [75] were invented. In 2012, the Wang group reported a new type of generator – triboelectric generator (TENG) – that can effectively harvest ambient mechanical energy by coupling triboelectric effect and electrostatic induction [76]. A typical TENG device consists of two materials with distinct electron affinities, and at the back of the materials, metal electrodes are deposited. When the two materials are brought into contact, electrons transfer from the side with lower electron affinity to the higher one, leaving the former surface positively charged and negatively charged on the later. When the two surfaces are separated, a potential difference over the two will be established, inducing free electrons in the metal electrodes at the backside to rebalance it, causing transient current in the external circuit. By varying the capacitance between the two electrodes, alternative current (AC) can be generated. TENGs have attracted broad interest over the past few years, exhibiting great potential in energy harvesting as well as self-powered sensing.

2.3.1 The theoretical model of TENGs

The first TENG was reported in 2012 [76], where two insulators, polyethylene terephthalate (PET) and Kapton, were used as triboelectric materials and brought into contact via bending, gold was deposited at the back of both materials, as shown in Figure 2-7. It was reported to generate an open-circuit voltage (V_{OC}) of 3.3 V and short-circuit current (I_{SC}) of 0.6 μA , the peak power density was $\sim 10.4 \text{ mW/cm}^3$. Since then, many studies have been devoted to TENG for mechanism researches and application developments.

Figure 2-7 Illustration of the structure and working principle the first reported triboelectric nanogenerator. [76]

The mechanism of TENGs can be traced from Maxwell's displacement current [77], which is defined as

$$J_D = \frac{\partial D}{\partial t} = \epsilon \frac{\partial E}{\partial t} + \frac{\partial P_s}{\partial t} \quad (2.1)$$

where D is the displacement field, E is the electric field, P_s is the polarisation field, ϵ is the permittivity of the medium. The first term $\epsilon \frac{\partial E}{\partial t}$ refers to a time-varying electric field that origins electromagnetic waves, while the second term $\frac{\partial P_s}{\partial t}$ refers to the polarisation field in materials. For TENGs, this time-varying polarisation filed rises from the external electrostatic charges when they undergo varying displacement.

As the fundamental working principle of TENGs is a combination of contact electrification and electrostatic induction, they can be analysed through the capacitive properties. For an arbitrary TENG, there is usually a pair of materials facing each other. At the back of the materials, metal electrodes are deposited to enable charge transfer. When the materials are forced to contact, contact electrification happens, and the electrostatic charges with the equal amount but opposite signs generated on both

surfaces respectively. With defining the amount of charge transferred as Q , one electrode would be occupied with a net negative charge of $-Q$ while the other with positive charge $+Q$. By varying the capacitance, a displacement current can be generated as $I = \frac{dQ}{dt} = C \frac{dV}{dt} + V \frac{dC}{dt}$.

Similar to capacitors, a potential difference $V_{OC}(x)$ is generated between the two polarised charged surfaces as a function of separation distance x . For a TENG, if an external circuit is connected, the electrons will be driven to flow to screen the potential difference. Hence the already transferred charge Q also contributes to the voltage output as $-Q/C(x)$, where C is the capacitance between the two electrodes. Therefore, the overall voltage difference between the two electrodes can be expressed as [78]

$$V = -\frac{1}{C(x)}Q + V_{OC}(x) \quad (2.2)$$

Eq. (2.2) is known as the V-Q-x relationship and is valid for any modes of TENGs. Under short-circuit conditions, the transferred charge Q_{sc} fully screen the potential difference, results in $V = 0$. Thus, the fundamental relationship of Q_{sc} , C and V_{OC} is given by

$$Q_{sc}(x) = C(x)V_{OC}(x) \quad (2.3)$$

The overall system can be represented by a series connection of an ideal voltage source and a capacitor. It is important to point out that TENG is a high-impedance charge source and its inherent impedance rises from its inherent capacitance, in order to maximize the power output and to neglect the effect from parasitic resistance from the metal electrodes, the inherent TENG resistance has to be high.

2.3.2 Four working modes of TENGs

Based by the fundamental electrostatic induction process, four different operation modes of the TENG are developed into, including vertical contact-separation mode, lateral-sliding mode, single-electrode mode, and freestanding triboelectric-layer mode, as shown in Figure 2-8.

Figure 2-8 The four fundamental modes of triboelectric nanogenerators: (a) vertical contact-separation mode; (b) lateral-sliding mode; (c) single-electrode mode and (d) freestanding triboelectric-layer mode. [79]

Vertical contact-separation mode

In the vertical contact-separation mode of TENGs, the relative motion of the surfaces is perpendicular to the interface, so that the potential difference variation is generated by altering the gap distance between the electrodes, as shown in Figure 2-8(a). Contact-separation mode is the basic mode of TENG, and it can be easily achieved in practice. Zhu et al.[80] reported a TENG consisting of a polymer later with nanoparticle gold

electrode operating in this mode, and it succeeded to generate an open-circuit voltage of 200 V, a short-circuit current of 2 mA and a power density of 313 W/m².

Lateral sliding mode

In the lateral sliding mode of TENGs, the potential difference variation is introduced via relative displacement parallel to the interface, as shown in Figure 2-8(b). When the top electrode is slid onto the bottom one, the tribo-charges on both dielectric surfaces in the overlapped region screen off the previously induced charge in the opposite metal electrodes. Via varying the overlapping areas of the surfaces, a potential difference will be generated, driving electrons to flow between the electrodes through the external circuit. The lateral sliding mode is often implemented as grating structured rotating devices. Zhu et al. [81] have reported a device delivering current density of 0.18 A/m² with 10 grating units that are 3 mm in length, and with an energy conversion efficiency of 8–31%.

Single electrode mode

To adapt to the situation where the device cannot be attached to an electric conductor, such as human walking and moving transportations, single electrode mode has been developed by connecting the bottom material to the ground, so that once the charged dielectric approaches or moves away from the bottom material, electrons can flow freely between the ground and the electrode to balance the potential difference variation, as shown in Figure 2-8(c). Bo Meng et al. [82] reported a polydimethylsiloxane (PDMS) film on a PET substrate with indium tin oxide (ITO) coated at the back, when tapped with a bare finger, a V_{OC} of up to 130 V and a short-circuit current density (J_{SC}) of about 1 $\mu\text{A}/\text{cm}^2$ were achieved. Several more applications such as harvesting energy from airflow [83], rotation tire [84] and even raindrop [85] have been demonstrated.

Freestanding triboelectric-layer mode

The freestanding triboelectric-layer mode of TENGs is developed from the single electrode mode where instead of using the ground as the reference, a pair of electrodes in connection is used, as shown in Figure 2-8(d). A typical design is to lay two symmetric electrodes underneath the tribo-layer separated, the free-moving tribo-layer causes asymmetric distribution of charges, inducing electrons to flow between the two electrodes to balance the local potential distribution [86]. This mode is favourable in applications for harvesting energy or sensing from a moving object while the entire system needs to be freestanding. A TENG using fluorinated ethylene propylene (FEP) in friction with two aluminium (Al) electrodes was reported to generate V_{OC} of 14 kV and J_{SC} of 3.2 mA/m² [87].

2.3.3 Strategies for improving performance of TENG

Theoretically, any two materials with distinct electron affinities can be paired to construct a TENG, but in order to optimise the highest amount of tribo-charge density obtained via contact electrification, materials farther apart on the triboelectric series table are preferred. Besides the selection of materials, there are majorly three strategies to enhance the charge density: material functionalisation, effective contact area improvement and operation condition optimisation.

One approach in material functionalisation is to modify the functional groups on the material surfaces for particular charge trapping ability. For example, Shin et al.[88] (in Figure 2-9(a)) reported two PET surfaces resulted in different triboelectric polarities by functionalising one surface with poly-L-lysine solution and the other with trichlorosilane (FOTS). With the functionalized PET films, a maximum V_{OC} of ~ 330 V and J_{SC} of ~ 270 mA/m² with high stability during more than one month were demonstrated. Alternatively, the charge density can be enhanced by integrating a

transport layer to introduce extra electron trap levels, which can facilitate the charge accumulation process and may shift the electron affinity of materials further apart. Reported in [89], the triboelectric charge density has been increased by a factor of 11.2 by introducing a composite structure of polystyrene (PS) and carbon nanotubes (CNTs) into polyvinylidene fluoride (PVDF), as shown in Figure 2-9(b). Another way is to manipulate the bulk composition with high dielectric properties for larger charge capacity. A TENG device using a composite sponge PDMS with 10% SrTiO_3 nanoparticle was reported with over 5-fold power enhancement compared with pure PDMS [90], as shown in Figure 2-9(c).

As for effective contact area improvement, one universal method is to introduce nano/micro-structures on the triboelectric materials, such as nanoparticles [80], nanowires[91], [92] and pyramid arrays via lithography [93], as shown in Figure 2-9(d). Also, soft materials such as silicon rubber were often used to assist the intimate contact with stronger deformation and to obtain higher charge density. Wang et al. [94] reported a tube-like silicone-based flexible TENG (shown in Figure 2-9(e)), with a proper design of the inner helix electrodes, a high charge density of $250 \mu\text{C}/\text{m}^2$ was generated. In addition, the effective contact area can be enlarged in liquid-to-solid contacts. Tang et al. [95] demonstrated the first liquid-metal-based TENG by moving the dielectric materials coated electrode in and out of liquid metal, as shown in Figure 2-9(f). The current generated was improved by four to five times than using a solid film electrode, and the instantaneous energy conversion efficiency reached 70.6%.

In order to find the ideal environment for TENG to perform, some researches have studied the influences of temperature, pressure and humidity. The results suggest that operating in extreme high temperature should be avoided, as shown in Figure 2-9(g), mostly due to the change in material permittivity and the formation of temperature-

induced surface defects, such as oxidation and defluorination, can severely decline the consequent charge density [96]. Also, from Figure 2-9(h), operating in low pressure is shown to be efficient to improve the performance. As air breakdown is one of the restrains in holding charges in TENGs, when operating in high vacuum, the maximum charge limited from air breakdown is elevated, resulting in higher charge accumulation and potential difference. Wang et al. [97] had reported a record of charge density at $1003 \mu\text{C}/\text{m}^2$ in vacuum, where the surface polarisation was achieved by coupling triboelectrification and hysteretic dielectric polarisation using an additional layer of a ferroelectric material. Furthermore, dry environment is more favourable for accumulating triboelectric charges, as shown in Figure 2-9(i), several studies have suggested that the water molecules may assist the self-discharge process on the surface [98], [99].

The three major solutions to boost the charges density is summarized in Figure 2-9.

Figure 2-9 Strategies to enhance charge density for improving output of TENG. Material functionalization (a) by modifying the functional groups on the surfaces [88]; (b) by functionalization (a) by modifying the functional groups on the surfaces [88]; (b) by integrating a transport layer [89]; (c) by manipulating the bulk composition with high dielectric properties [90]. Through effective contact area improvement (d) by introducing nano-structures [93]; (e) by incorporating soft materials [94]; (f) by using liquid metal electrode [95]. Through operation condition optimisation (g) of temperature [96]; (h) of vacuum [97]; (i) of relative humidity [98].

2.3.4 Power management

TENGs generate high voltage but low current in AC pulse form, and when converting mechanical energy from the ambient environment, the outputs are usually irregular. Besides, TENG is equivalent to a voltage source with large impedance due to its

mechanism introduced previously. Hence, low charging rate and power conversion efficiency make TENG inappropriate to drive conventional electronics directly.

Early studies had focused on direct integration of TENG with a secondary energy storage unit such as supercapacitors and batteries via rectifiers [100]–[102], but due to the impedance mismatching and the pulse charging, the energy loss is significant. It is vital to match the load resistance R_L to the internal impedance R_{in} of TENG. As TENG is equivalent to a voltage source in series with a large internal resistor R_{in} , when connecting to an external load R_L , the power P delivered to R_L is $P = IV = I^2 R_L = \frac{V}{(R_{in} + R_L)^2} R_L$, which is maximized when $R_L = R_{in}$.

Alternatively, DC convertor systems including a transformer, a rectifier, a voltage regulator and capacitors were used to convert the AC to DC current, but the conversion efficiency was low [103]. In some later applications, the generated electrical energy was stored in an energy storage unit before applying to electronics. For example, in [104], a temporal capacitor C_{temp} was connected with some switches, such that the C_{temp} would be charged to an optimal voltage, then the switches would be turned on to allow the C_{temp} to discharge to the final energy storage unit through two coupled inductors. By optimising the capacitance of C_{temp} and the timing of switches to open or close, a total storage efficiency of 60% was achieved, which is about two orders higher than direct charging.

Meanwhile, as the highest achievable voltage on the energy storage unit is usually much lower than the open-circuit voltage of TENG, and only partial induced charges are transferred, there is a huge waste regardless of the energy conversion efficiency. Hence, a smart charging cycle is necessary to ameliorate the energy storage performance. The study has shown that the energy output per cycle E is determined by the enclosed area

of the built-up voltage V and the transferred charge Q for each stage during operation, denoted as $E = \bar{P}T = \int_0^T VIdt = \int_{t=0}^{t=T} VdQ = \oint VdQ$ [105], where $\bar{P}$ is the average power within a period T . Base on this mechanism, a rational designed cycle was proposed to short-circuit connect the electrodes at $x=x_{\max}$ (furthest apart) and $x=0$ (overlapped), so that the charge transferred maximised, and the maximum energy storage efficient was improved to 50% [106].

2.3.5 Major applications

Energy harvester

One major application for TENGs is to harvest low-frequency energy from the ambient environment such as human activities, vibrations from wind energy and water energy. For example, a TENG was integrated with a backpack for harvesting the vibration from human walking, where the Al and Polytetrafluoroethylene (PTFE) surfaces move relatively to each other during human walking, generating an open-circuit voltage up to 428 V and a short-circuit current of 1.395 mA, the peak power was reported up to 30.7 W/m² [107]. Also, Wang et al. [94] fabricated an outsole with TENG to harvest walking energy for powering wearable electronics. Shown in Figure 2-10(a), the device was fabricated with tube-shaped elastomeric materials, and on the inner wall of the tube, a helix inner electrode was adhered, such that when the tube was pressed, the inner electrode would move relative to the dielectric layer, generating electricity. The energy generated was demonstrated to power up a digital watch while jogging.

Wind energy is another substantial source awaiting to be harvested. The primary TENG for harvesting wind energy [83] was built with an acrylic box with two Al foils on the bottom and top inside, and in the middle of the box, an FEP film was attached at one end so that it could vibrate along with the wind and contact the Al foils. With a wind speed of 10 m/s, the devices managed to generate high voltage at 100 V and current of

1.6 μA . A more efficient design of TENG is shown in Figure 2-10(b), where the vertically stacked structure and flexible polymer membranes were used, such that when the wind flew into the device, the membranes randomly contacted and separated with the electrodes, generating electricity [108].

Another trend in TENG is to harvest energy from water, due to the liquid-solid electrification, the raindrop can be directly used as they obtain charges from the air and hence generate current from electrostatic induction when dropped on the surface [109], [110]. To make use the kinetic energy inhabited in water waves, shown in Figure 2-10(c), a fully enclosed spherical TENG was designed, inside which there were electrodes attached on the inner shell, and a dielectric ball was free to roll within the shell. This TENG can float on the water and under the motion of waves, a peak current of 1 μA was generated [111], suggesting a promising solution to harvest the energy from tides in large scale.

Figure 2-10 TENG applications in energy harvester (a) from biochemical energy when walk [94]; (b) from wind energy [108]; (c) from water energy [111].

Active sensor and self-power sensors

Another application field is to use TENGs as active sensors based on the direct transform from mechanical stimuli to electric signals. These sensors usually consume less stand-by power supplying and can be integrated with less complicated control systems such as passive transistors. The first self-powered pressure sensor with TENG was fabricated

with PET in contact with PDMS, with introducing pyramid surface patterns on the PDMS film, light pressures such as a water droplet (~ 3.6 Pa) and even a falling feather (~ 0.4 Pa) were detectable [112]. Based on this structure, application in pressure imaging/mapping with Light-emitting diodes (LEDs) for visualisation was developed, such that when an object was placed within the sensing region, the surfaces came to contact under the pressure and generated current, lighting up the corresponding LEDs [113]. In [93], as shown in Figure 2-11(a), multiple TENG units consisting of patterned PDMS film in contact with silver nanowires were integrated into a sensing panel, by fitting V_{OC} and I_{SC} characteristics with applied pressure, the sensing panel could detect the pressure distribution with fast response (< 5 ms) and low detection limit (2.1 Pa).

TENGs are good candidates for applications as vibration sensors. Shown in Figure 2-11(b), Wang et al. [114] reported a resonator structure that could sense the amplitude and frequency of vibration. The resonator consisted of a FEP film in between two Al electrodes, the two materials were separated with springs, and the magnitudes of V_{OC} and I_{SC} detected were in linear correlation of the vibration amplitude and speed, so that the quantitative information about the vibration could be extracted. The vibration from acoustic waves was also detected using TENG active sensors[115]–[117]. An acoustic sensor based on TENG was reported in [115], where the FEP films and flexible membrane with gold (Au) deposited were used and separated with a tiny gap. As the membrane deformed and vibrated according to the air pressure variation caused by the acoustic waves, the induced current could be correlated to the frequency, showing high sensitivity and adjustability by simply designing the geometry of the membrane.

TENGs are also developed as motion sensors to determine the position of an object along the time or to identify human body movements. To accurately track an object, Su et al. [118] reported a single-electrode-based TENG sensor constructed with a PTFE

tube with an array of copper ring electrodes on the outer surface, with specific gap separated adjacently, as shown in Figure 2-11(c). When an object passed by the electrodes, pulse currents were generated in succession due to the electrostatic induction, and the mechanical motion of the object can be then determined in real-time by analysing the pulse intervals.

Figure 2-11 TENG applications in active sensors as (a) pressure sensors [93]; (b) vibration sensors [114]; (c) motion sensors [118].

Since the emerging of TENG in 2012, it has been developing rapidly. Applications ranging from self-charging power system in both micro and large scale to self-powered sensors have been realised. TENGs have been applied in different fields, and there is still vast knowledge to research on.

2.4 Theory in semiconductor devices and p-n junction

Solid-state materials are commonly divided into insulators, semiconductors and conductors according to their increasing conductivities. As the conductivity of a semiconductor can be modified with material types, impurity levels, temperatures, illumination and more, the semiconductor becomes an important material in all modern electric applications. A semiconductor is commonly used with impurities doped. An n-type doped semiconductor is achieved by substituting the original atoms with the ones have more valence electrons, in a way that they “donate” additional electrons to the conduction band. Similarly, a semiconductor can be p-type doped by replacing with atoms with fewer valence electrons that “accept” electrons and release holes in the valence band. By introducing donor or acceptor impurities, the electron or hole concentrations increases, which leads to the change in conductivities. For an intrinsic semiconductor, its energy of the Fermi level (E_i), the energy level where the probability of being filled with electrons is 50%, is usually considered to lie in the centre of the energy gap. And for doped semiconductors, shown in Figure 2-12(a), their Fermi levels (E_F) lie away from E_i depending on the doping concentration, with [119]

for n-type,

$$E_i - E_{FN} = -kT \ln\left(\frac{N_D}{n_i}\right) \quad (2.4)$$

and for p-type,

$$E_i - E_{FP} = kT \ln \left(\frac{N_A}{n_i} \right) \quad (2.5)$$

where E_{FN} and E_{FP} are the Fermi levels in n-type and p-type semiconductors respectively, k is the Boltzmann constant, T is the absolute temperature in degrees Kelvin, n_i is the intrinsic carrier density, N_A and N_D are the concentrations of acceptors and donors respectively. In other words, the E_F lies closer to the valence band edge in p-type doped semiconductor while it lies more towards the conduction band edge in n-type.

Figure 2-12 (a) Energy band diagram for individual uniformly doped p-type and n-type semiconductors. (b) Energy band diagram of a p-n junction at thermal equilibrium.

A p-n junction is formed when the n-type and p-type semiconductors are joined. When the n-type and p-type semiconductors are in contact, the concentrations of carriers change abruptly, and electrons instantly diffuse from n-type semiconductor to the p-type while holes diffuse from p-type semiconductor to the n-type. However, this diffusion results in a positive space charge region in the n-side and a negative region in the p-side, which form an electric field in the direction opposite to the diffusion current, such that at thermal equilibrium, the drift currents under the electric field exactly cancel the diffusion currents, yielding zero net currents across the junction and one aligned Fermi level. This region is also called depletion region, or p-n junction. At thermal equilibrium,

shown in Figure 2-12(b), the total potential difference over the region, or called the built-in potential V_{bi} [119]:

$$V_{bi} = \frac{1}{q}(E_{FN} - E_{FP}) = \frac{kT}{q} \ln \left(\frac{N_A N_D}{n_i^2} \right) \quad (2.6)$$

Assume the charges are fully ionized in the depletion region, the charge density in the depletion region in the n-side is qN_D , and that in the p-side is $-qN_A$. The depletion regions extend for a width of W_n in the n-side and W_p in the p-side with $N_A W_p = N_D W_n$ according to overall charge neutrality, where W_n and W_p can be determined via [119]

$$W_n = \sqrt{\frac{2\epsilon_s}{q} \frac{N_A V_{bi}}{N_D(N_A + N_D)}} \quad (2.7)$$

$$W_p = \sqrt{\frac{2\epsilon_s}{q} \frac{N_D V_{bi}}{N_A(N_A + N_D)}} \quad (2.8)$$

And the total depletion width W [119]:

$$W = W_n + W_p = \sqrt{\frac{2\epsilon_s}{q} \left(\frac{N_A + N_D}{N_A N_D} \right) V_{bi}} \quad (2.9)$$

When a voltage V is applied to a p-n junction, the balance between the drift current and diffusion current will be disturbed. When V is positive at the p-side with respect to the n-side, or called forward bias, the electrostatic potential across the depletion region reduces to $V_{bi} - V$, which corresponds a lower energy barrier for electrons to overcome to diffuse from the n-side to the p-side. While a negative V , or reverse bias, increases the electrostatic potential to $V_{bi} + V$, and leads to a reduced diffusion current. However, as the drift current depends on the minority carriers, it varies insignificantly with V . This dependency results in the rectification characteristic of a p-n junction that current is allowed only in one bias direction but not the other, which is represented as [119]

$$I = I_S \left(\exp \left(\frac{qV}{kT} \right) - 1 \right) \quad (2.10)$$

where I_s is the saturation current, V is the bias voltage applied to the junction.

The capacitance of the junction per unit area C_j is defined as the variation in charge under the incremental in V , and for an abrupt junction where the doping concentration in one side is much higher than the other, C_j can be expressed as a standard parallel-plate capacitor with a gap distance equal to the depletion width W [119]:

$$C_j = \frac{\epsilon_s}{W} = \sqrt{\frac{q\epsilon_s N_B}{2(V_{bi}-V)}} \quad (2.11)$$

where N_B is the lightly doped bulk concentration.

An important application of p-n junction in energy harvesting is the solar cell. When illuminating a p-n junction, photons with enough energy can break bonds in the crystal and generate electrons and holes. However, for those electrons and holes generated in the junction region, the built-in electric field separates the electrons to the positive region in the n-side and holes to the negative region in the p-side, resulting in a current across the junction flow from n-side to p-side. As this light generated current I_L flows across the junction in the opposite direction to the forward-biased current for the p-n junction in dark, the $I - V$ rectification curve of a solar cell becomes [119]

$$I = I_s \left(\exp\left(\frac{qV}{kT}\right) - 1 \right) - I_L \quad (2.12)$$

Correspondingly, the open-circuit voltage V_{OC} is obtained at the forward bias voltage where the forward bias current equals to the light generated current and is determined by [119]

$$V_{OC} = \frac{kT}{q} \ln\left(\frac{I_L}{I_s} + 1\right) \cong \frac{kT}{q} \ln\left(\frac{I_L}{I_s}\right) \quad (2.13)$$

To get the most power from a solar cell, it is important to load a matched resistance in the external circuit, so that the maximum power P_m can be delivered with the optimal current I_m and optimal voltage V_m . P_m can be calculated from [119]

$$P_m = I_m V_m \cong I_L \left[V_{OC} - \frac{kT}{q} \ln \left(1 + \frac{qV_m}{kT} \right) - \frac{kT}{q} \right] \quad (2.14)$$

The technology for solar cells has been developed along the time, while solar cells are becoming an important candidate for renewable energy supply, there are still many challenges remained such as to improve the conversion efficiency and reliability. Also, expensive energy storage systems are always needed as the power generation is essentially weather dependent and only available in the daytime. Also, there are environmental impacts raised from solar cells, such as pollutions and habitat loss due to massive installation area and toxic materials used in the production.

Chapter 3   Metal Ion Detection in Aqueous Solutions

3.1   Introduction

With inevitable pollution resulted from highly industrialised development, the concern of health issues raised from contaminated drinking waters is increasing, leading to the demand for all kinds of water sensors. One of the most well-recognised methods employed in water sensors is to use inductively coupled plasma mass spectrometry (ICP-MS), which ionizes the samples and can detect the elements at very low concentration [120], [121]. Another standard technique for determining the concentration of elements in the samples is to apply atomic absorption spectrometry (AAS), which is based on the absorption of light by free metallic ions [122], [123]. Nowadays, methods without spectroscopic techniques are also gaining popularity, such as through electrochemical techniques [124]–[126] or by applying particular nanomaterials [127]–[129]. In the electrochemical techniques, where two or three electrodes in contact with the sample, the presence of certain ions can be determined by analysing the oxidation/reduction reactions occur at the working and counter electrodes. Adding nanomaterials, such as quantum dots and metal nanoparticles, is used for surface functionalization and high sensitivity in some water sensors. Overall, current techniques are adequately sensitive and accurate in detection. However, they, in general, require expensive equipment, dedicated sample pre-treatment and/or analyte pre-concentration steps.

Current existing hazards to water are mostly originated from industrial, chemical and biochemical pollutants, as a matter of fact, these contaminants usually contain charged particles [130]. Hence, the detection of the charge concentrations in a water sample can

be a valuable criterion to identify presence of chemical or biological contamination [131]. As contact electrification exists between solid-liquid materials, the dependence of the resultant triboelectrification on the existing charged particles in the water samples may serve as sensing characteristics.

Herein, in this chapter, we developed a water sensor for detecting ion concentration in water samples based on electrostatic methods. The mechanism and performance are discussed. It could perform rapid detection of charged particles concentrations and the pH range and hence predict water drinkability.

3.2 Experimental setups and mechanism

PET film was used in this study because of its hydrophobic property and high electron affinity in the triboelectric series [51], and it is commonly used for commercial beverage containers. A 4 cm $\times$ 4 cm PET film was dipped in water samples up and down repetitively and loaded in a holder without further touching the centre region. Thanks to the hydrophobicity, no visible water droplets remain on the surface when the film was pulled out from water samples. A 2 cm $\times$ 2 cm titanium (Ti) plate connecting to a current meter was used as the electrode and was fixed on the translation stage of a linear motor. The metal plate was then controlled to approach or pull away the PET film with their centre aligned. The gap between the PET film and the metal plate was from 1.0 mm to 11.0 mm (see Figure 3-1(a)).

Figure 3-1(b)-(e) illustrate the sensing processes. As PET has a higher electron affinity than air according to the triboelectric series [51], it tends to gain electrons and gets negatively charged in the air. When there is no relative movement, no current flows in and out the Ti plate (Figure 3-1(b)). When Ti plate starts to approach to the PET film, some electrons in the Ti plate are repelled gradually by the negative surface charge on

the PET film, inducing a negative current flowing in the external circuit (Figure 3-1(c)) until the gap variation stops (Figure 3-1(d)). When the Ti plate is pulled away from PET, the electrons flow back to the Ti plate to balance the potential difference, inducing a positive transient current (Figure 3-1(e)). The total amount of charge transferred during each charging and discharging processes is determined by the absorbed ion charge density on the PET film, Ti plate area and the gap distance variation. When the PET film is dipped in a water sample, triboelectrification between the liquid and the film redistribute triboelectric charges on the surface. Depending on the properties of the ions in the liquid, the absorbed charge density on the PET varies, which can be detected based on electrostatic induction.

Figure 3-1 Schematics of the sensing process. (a) Experimental setups; (b) initial position where Ti plate is 11 mm away from PET film; (c) Ti plate approaching to PET film; (d) Ti plate reaches the smallest gap of 1 mm; (e) Ti electrode moving back to the initial position.

Several liquid samples were prepared and tested, i.e. deionised (DI) water, solutions of Ca^{2+} (prepared from CaSO_4) , Co^{2+} (from $\text{Co}(\text{NO}_3)_2$), Cr^{3+} (from CrCl_3) , Fe^{2+} (from $\text{Fe}(\text{NO}_3)_2$) , Mg^{2+} ions (from MgCl_2), Ni^{2+} ions (from $\text{Ni}(\text{NO}_3)_2$), Zn^{2+} ions (from $\text{Zn}(\text{NO}_3)_2$), Na^+ ions (from NaHCO_3), acidic samples from HCl and alkaline samples from KOH . Each chemical was diluted from its initial concentration of 0.1 mol/L until its detection limit was reached, such that the detected current signals were indistinguishable from the signal obtained from DI water. Furthermore, water samples from household sewage, reservoir and sea beach were tested using this sensing method.

3.3 Results and discussion

3.3.1 Contact electrification in air and liquid

The Ti plate was controlled to move from 11 mm to 1 mm from the PET film. While the Ti plate approaching the PET film, negative pulses were generated. During the separating, positive pulses with comparable magnitudes were generated. Figure 3-2 show two arbitrary cycles of the current and charge generated in the external circuit before (Figure 3-2(a)) and after (Figure 3-2(b)) dipping in the DI water up and down more than ten times. The directions of the current indicate that the PET surface was negatively charged in both conditions. However, the amount of charge transferred reduced from 1.1 nC to 45 pC after dipping. The reduction in surface charge can be interpreted from contact electrification between PET and air/water. As mentioned previously, PET is negatively charged in air due to its higher electron affinity, but when it is dipped in DI water, liquid-solid contact electrification results in redistribution of surface charge on the PET film [43], [132]. Because of that water has an average higher electron affinity than air, PET gains less electrons from air than from water, resulting in less negatively charged surface after dipping in water.

Figure 3-2 Instantaneous current and charge generated when approaching and separating a Ti plate from (a) dry PET film and (b) PET film after dipping in DI water.

It is worth to note that although the overall charge of a water molecule (H_2O) is electrically neutral, the difference in the electronegativity between hydrogen and oxygen causes an electric dipole moment, and the auto-dissociation of water leads the formation of hydronium ion (H_3O^+) and hydroxide ion (OH^-) in the water [133]. As the dry PET film is initially negatively charged in the air, when it is just dipped in water, some of the negative surface charges may be randomly neutralized by the positive H_3O^+ , resulting in decreased net charge density, rather than the accurate electrification results with water. Hence, sufficient times of dipping in water is necessary to reduce the influences of those pre-existing static charges. Figure 3-3 shows a set of currents after dipping the PET film in the water multiple times. The current peaks were observed to decay for the first few rounds due to the partial neutralization of the auto-dissociated water molecules and gradually reached a stable value.

Figure 3-3 Current generated after dipping PET film in DI water multiple times.

3.3.2 Detection of Metal Cations

Solutions with different concentrations of metal ions were prepared (see Section 3.2) and used in the experiments for the PET films to dip in. Figure 3-4 shows the short-circuit current I_{SC} detected after being dipped in $\text{Fe}(\text{NO}_3)_2$ solutions with different concentrations. The peak value of I_{SC} decreased with higher concentrations of Fe^{2+} and eventually diminished to the noise level. The decrement can be interpreted from two aspects: reduction in electron transfer and charge screening. According to Lin et al [134], electron transfer and ion transfer exist concurrently in contact electrification between solid and liquid. For hydrophobic surfaces where the interaction between water molecules and the surface is weak, electron transfer dominates the contact electrification. When the solution concentration increases, the electron transfer can be hindered due to a faster self-discharge that originated from the decreased dielectric constant of the solution. As a result, the final triboelectric charges obtained by the surface reduced with higher concentrations of ions. On the other hand, despite the hydrophobicity of PET film, a tiny amount of moisture may still adhere on the film after dipping, so that the charges within the residual electrolytes cause a partial screening of the triboelectric

charges on the PET film, which is also adverse for the final triboelectric charges to be detected [135].

Figure 3-4 Current generated after dipping the PET film in $\text{Fe}(\text{NO}_3)_2$ solutions with increasing concentrations.

As PET film is originally negatively charged, the effect from added cations dominates the final triboelectrification rather than the anions. The solutions were successively diluted until their detection limit was reached, such that the detected current signals are indistinguishable from that measured for DI water. Figure 3-5 shows the average amount of charges detected from PET film after dipping in solutions with various metal cations at different concentrations. A general trend of decreasing amount of charges detected from the PET film after dipping in higher concentration solutions was observed. Nevertheless, for metal cations with the same charge, the output values were different. The difference can be attributed to two characteristics of the cations: electronegativity and affinity to the PET film. Electronegativity refers to the ability of the cation in attracting a bonding pair of electrons, which could affect the strength in absorption of negative charges on the PET film surface. Based on Pauling's scaled electronegativity [136], the order of ions with ascending electronegativity is: Na (0.93), Ca (1), Mg (1.31),

Zn (1.65), Cr (1.66), Fe (1.83), Co (1.88) and Ni (1.91). This sequence is broadly consistent with the strength in reducing negative charges on PET surface, such that with the same concentrations, more electronegative cations tend to result in a smaller amount of charge detected from the PET after dipping, and thus a smaller detection limit can be reached in general. This is because that with a higher electronegativity, the cations are stronger in binding with the negative charges on the PET surfaces, which reduces the overall charge remained on the surface [137]. However, the electronegativity and charge reduction ability do not completely align. For example, Ni and Co have the highest electronegativity but are moderate in gaining negative charges from PET surface among the tested cations. This variation could be caused by the different affinities of the cations to the PET surface, such that cations with higher affinities to PET film can have more intimate contact with the film, and hence acquire more negative charges, resulting in less charge detected from PET after dipping. Some of the cation detection limits are summarized in Table 3-1, with the reference of the concentration range for drinking recommended by WHO. For all the ions tested in this work, the detection limits cover the recommended concentration range. At the upper limit of recommended ion concentrations, the amount of charges detected were at least 18% lower than that from DI water. Thus, our approach could be employed as an indicator to predict the drinkability of water samples.

Figure 3-5 Normalised charge obtained after dipping PET films in water samples with various concentration of metal cations.

Table 3-1 Detection limits of metal cations in comparison to the recommended concentration for drinking

Metal ion	Recommended Concentration Range [138]	Detection limit	Normalised charge at the upper limit
DI water	-	-	1
Co²⁺	1 – 10 ppb	0.5 ppb	0.58
Cr³⁺	1 – 10 ppb	4 ppb	0.76
Ni²⁺	7.7 – 16.6 ppb	6 ppb	0.82
Ca²⁺	100 – 300 ppm	0.5 ppm	0.36
Mg²⁺	< 50 ppm	10 ppm	0.49
Na⁺	20 – 250 ppm	10 ppm	0.36

3.3.3 Detection of pH Values

This method was tested with acid (alkaline) solutions prepared from HCl (KOH). Figure 3-6 shows the trend of charge detected after dipping the PET film in solutions with pH

value from 1 to 13. It shows that for acid solutions ($\text{pH} < 7$), with increasing acidity, the negative charge detected from PET film reduced. When the acidity was sufficiently strong ($\text{pH} < 3$), positive charges increasing with stronger acidity were detected. As have discussed previously that the PET film is originally negatively charged in air due to triboelectric effect, there would be pre-existing charges on the surface when interacted with liquids. When dipped in acidic solutions, where the concentration of protons (H^+) is high, the pre-existing negative charges on the PET surface are gradually neutralised by H^+ , resulting in decay in charge detected. Furthermore, according to Lewis acid-base theory that an acid tends to gain electrons, the massive amount of H^+ in the strong acidic solutions may even gain electrons from the PET film, leaving the PET surface positively charged. On the other hand, when dipping the PET film in alkaline solutions ($\text{pH} > 7$), where an excessive amount of OH^- present, the net negative charge detected was observed to decrease with increasing alkalinity. This could be caused by auto-dissociation of water near the interface between liquid and PET film. As PET surface is originally negatively charged, the pre-existing negative charges repel the OH^- away from the surface. Meanwhile, the auto-dissociation of water generates more H^+ ions [139], [140], which increases the local concentration of H^+ and in turn reduces the overall negative surface charge on the PET in the way similar to acidic solutions.

The pH range of drinking water recommended by WHO is 6.5 – 9.5 [138], corresponding to a normalised charge of 0.73 ($\text{pH} = 6.5$) and 0.64 ($\text{pH} = 9.5$) detected with this method. For solutions beyond the recommended pH range, the amount of charge detected is at least 26.7% lower than the value detected from DI water. This suggests that our technique can be employed as a proper indicator to identify the drinkable pH range of water samples.

Figure 3-6 Normalised charges detected with PET dipped in solutions of increasing pH values.

3.3.4 Tests of water samples collected from the environment

The method was applied in water samples retrieved from a local reservoir, sea beach and household drain. Figure 3-7 shows the charges detected with water samples mentioned above with being diluted in DI water at a different ratio. For reservoir water, lower than 0.45 normalised charge was detected. However, mixing DI water with the reservoir water brought up the amount of charge: at a ratio of (DI water)80: (Reservoir water)20, the value rises to 0.73 and approaches to the requirement to be potable set according to our sensor. As for sea water, the extremely low charge amount denies its drinkability even after diluting at a ratio of (DI water)80: (sea water)20, which is consistent with the fact that sea water contains high concentrations of metal cations and pollutants. For household drain water, a reversed charge polarity was observed, indicating the water is unsafe to drink, which may be due to more complicated chemical charges and bacteria inside. Although our technique is not capable of differentiating metal ions mentioned here, it can serve as a fast screening test.

Figure 3-7 Charge detected from reservoir water, sea water and drain water at various dilution

3.4 Conclusions

In this chapter, a water sensor for metal ion detection based on liquid-solid contact electrification and electrostatic induction was developed. The surface charge remained on the PET film after contacting with a solution decreases linearly with increasing ion concentration. It has been found that the detection limit of each type of metal ions depends on the electronegativity of individual ions as well as their adhesion behaviour to the PET film, which can serve as a water sensor for metal ion detection. Also, the surface charges detected from the PET film reduce with increasing either acidity or alkalinity of the solution for dipping. This sensor can be applied for quick assessment of the drinkability of a water sample in terms of metal ion contamination and pH range. Although the selectivity of the sensing method is inadequate, its sensitivity is high. Future studies combining filtration with proper selection of the pore size or acting agent of the targeting metal ions can be potential solutions to optimise this sensing technique.

Chapter 4   Triboelectric Generators

4.1   Introduction

Triboelectric nanogenerators (TENGs), were invented by Wang's group in 2012 [76], are a type of generators to convert mechanical energy to electrical energy based on triboelectrification and electrostatic induction. A conventional TENG device typically consists of two materials, usually at least one is insulator, with metal electrodes deposited at the back. These two materials are with distinct electron affinities, so that when they contact, electrons transfer from the material with lower electron affinity to the other, leaving the two materials oppositely charged on the surfaces. When the two surfaces are separated, transferred charges are stuck on the surfaces as electrostatic charges, inducing electrons in the back electrodes. Thus, a potential difference is established over the two electrodes. By modulating the capacitance formed between the electrodes, such as relative motion, the potential difference changes, driving electrons flow through the external circuit under electrostatic induction. With periodic capacitance variation, alternative current (AC) is generated, converting mechanical energy into electrical energy.

In this chapter, some surface modification methods were employed on simple-structured TENGs to enhance the performance, including using pressed metal foams as contact electrodes, polishing contact surface with sandpaper, processing contact materials with oxidation and reduction reaction. Also, the influences of contacting force, contacting time, load resistance and operation frequency were studied. The drawbacks of the TENGs are discussed.

4.2 Experimental setups and device fabrication

There are many designs of TENG structures to suit for different applications, in this chapter, simple structures adapted from vertical contact mode with either single or double electrodes were fabricated. Figure 4-1 shows the schematic graphs and photographs of the three structures used in the work. Structure I was a two-electrode fold-up structure, where a dielectric film was used as the substrate and folded along the centre. Two pieces of metal tape were pasted on the opposite sides of the overlapped area, such that when the device was pressed, the metal surface on the lower layer would touch the dielectric surface of the upper layer, as shown in Figure 4-1(a). Structure II was a modified structure based on Structure I, where a wider piece of dielectric film was folded into a zigzag shape with even intervals, and the metal electrodes were taped alternatively on the upper or the lower surfaces of the dielectric film. Structure II assembled multiple TENG units in stack, so the dielectric surface in all segments could touch one adjacent metal surface under pressing. This stacking design managed to enlarge the contact area without sacrificing to take up more space. Structure III was designed in single-electrode mode, and it consisted of a metal foil and a dielectric film wrapping around the metal as shown in Figure 4-1(c). When the device was pressed, the dielectric film on both sides contacted with the centre metal and became charged once separated. This structure required a connection to the ground, so that the electrons flowed between the metal and ground, generating current. When the pressure was released, the dielectric films intended to revert to their original curvature due to their resilience, which naturally separated after releasing.

Figure 4-1 (a) Schematics and (b) photograph of the two-electrode fold-up structure; (c) schematics and (d) photograph of the multi-layer fold-up structure; (e) schematics and (f) photograph of the wrapped single electrode structure.

The as fabricated devices were attached onto a sample holder, behind which a force gauge was installed. A linear motor was controlled to press and release the device repeatedly. A photo of the whole setup and measuring system is shown in Figure 4-2 Experimental setup for contact/separate experiments, including a linear motor, sample holders, force gauge and measurement systems.

Figure 4-2 Experimental setup for contact/separate experiments, including a linear motor, sample holders, force gauge and measurement systems.

4.3 Performance enhancement with surface modification

Based on the mechanism of TENGs discussed in Section 2.3, the amount of charges generated in each cycle is associated with the resultant triboelectrification charges on the surfaces. One essential element to evaluate the efficiency of triboelectrification is the charge density, which is determined by the total amount of charges and the apparent contact area. Although the tendency of electron transfer is dependent on the relative electron affinity difference of the materials, how much charge can be transferred is affected by the actual contact area. As discussed previously in Section 2.1, the contact between two surfaces is always limited among asperities, surface modifications for asperity contact enhancement are desirable. To increase the roughness of either surface is a common approach, such as incorporating metallic nanoparticles on the contact electrode [80], [141]–[143], applying inductively coupling plasma (ICP) [114], [144]–

[146] or creating surface texture through lithography [112] to obtain nanostructure on the contact surface. Apart from those reported dedicated processes, in this work, we show several methods that increase the charge density efficiently.

4.3.1 Porous structured contact electrode using metal foams

A wrapped single electrode structured TENG consisting of a 2 cm × 2 cm nickel (Ni) foil in centre of the Kapton film was fabricated. The linear motor was controlled to press the device at 5 N and hold for 1 second before releasing. The press/release frequency was 0.5 Hz. When the two surfaces are contacted, the electrons in Ni foil transfer to the Kapton surface, resulting in Ni foil positively charged while the Kapton surface negatively charged. At the separation, a potential difference is established, inducing electrons to flow from the ground to the Ni foil through the external circuit, generating a positive transient current. When the two surfaces are contacted again, the negative electrostatic charges on the Kapton surface repel the electrons in Ni foil to rebalance the electrostatic field, inducing another transient current flowing in the opposite direction. With repeating mechanical motions, a stable AC signal could be observed. Occasionally, opposite pulses appeared at the end of separation, this is because that the sudden release of contact pressure allowed the Kapton and Ni to relax asynchronously, which resulted in relative motion after linear motor stopped, and induced minor pulses in the circuit. A Ni foam with the pore size of 200 μm and thickness of 1 mm was used as the electrode too, after which, the foam was then pressed down to 50 μm thick using the coin cell crimping machine and replaced the electrode.

Figure 4-3 show the microscope images and their short-circuit current (I_{SC}) output with Ni foil (ab), Ni foam (cd) and pressed Ni foam (ef) used as the centre metal electrode, respectively. The peak of generated using plain Ni foil was 27 nA, whereas that generated with the Ni foam was only 14 nA. With the pressed Ni foam, the I_{SC} increased

to 34 nA, nearly 30% higher than with the plain Ni foil. Need to mention that, due to the electrostatic shielding effect in metal, the electrostatic field within the conductor should be zero, so that the electrostatic charges can be regarded as evenly distributed within it rather than being confined on the surface. Therefore, increasing the surface area of a metal electrode would not affect its charge density directly. But introducing porous structure to the contact metal electrode can potentially enhance the asperity contact and thus possess an enlarged contact area. However, with a pore size of 200 μm , the actual contact area was limited at the protruding parts of the foam, which was far less than the plain Ni foil. After being pressed down to a thickness of 50 μm , the outmost surface became more compacted and the actual contact area increased. Besides the benefits from microstructure topology, the effect from the increased local pressure at the protruding parts could also contribute. Comparing to the plain Ni foil, the protruding parts on the pressed foam had higher pressure and a closer distance between asperities of the two surfaces. According to [147], reduced contact distance between polymers and metal can lead to electron gaining at not only the lowest unoccupied molecular orbit (LUMO) but also in other non-LUMOs regions due to the strong interface interaction. As a result, the final charge density was enhanced.

Figure 4-3 Surface modification using porous structured metal electrodes for $2\text{ cm} \times 2\text{ cm}$ wrapped single electrode structured TENG made of Ni and Kapton film. (a) Microscope image of Ni foil, and (b) the I_{SC} with contact force of 5 N; (c) Microscope image of 1 mm thick Ni foam with $200\text{ }\mu\text{m}$ pore size and (d) I_{SC} with contact force of 5 N; (e) Microscope image of the Ni foam that was pressed to a thickness of $50\text{ }\mu\text{m}$ and (f) I_{SC} with contact force of 5 N.

4.3.2 Oxidation and reduction for fine porous structures

For the same wrapped single electrode structured TENG with a $2\text{ cm} \times 2\text{ cm}$ Ni foil and Kapton, the Ni foil was performed with oxidation and reduction processes to introduce

fine porous structures. As illustrated in Figure 4-4(a), the Ni foil was first annealed in air at a temperature of 200 °C for 8 hours to form nickel oxide (NiO), followed by another round of annealing at 800 °C under the gas flow of a mixture with hydrogen and argon for 30 mins for the reduction process. From the scanning electron microscope (SEM) images in Figure 4-4(b)(d), a refined porous surface had been observed. The current generated using the plain Ni foil and the treated foil as the contact electrode are shown in Figure 4-4(c)(e). Under the same contact force of 5 N, the peak current increased from 27 nA to 55 nA, owing to the contact area enhancement from the new fine porous surface. Another factor may be associated with the incomplete reduction process in NiO. According to [148], [149], NiO is more positive than Kapton in the triboelectric series, where NiO had an average triboelectric charge density of 0.53 $\mu\text{C}/\text{m}^2$ after contact electrification with liquid mercury, whereas that value for Kapton was -92.88 $\mu\text{C}/\text{m}^2$. As a result, the remaining NiO particles contribute to additional electron transfer.

In addition, although the amount of charge transferred during separation and contact were the same, which was consistent with the mechanism of electrostatic induction, the magnitudes of I_{SC} were different for the two processes. This difference was clearly due to their unequal durations for charge flow. One possible reason is that after forming the porous surface, a thin oxide layer or defects were unavoidable, and the capacitance formed between the surface and bulk may prolong the charge induction, resulting in variation in magnitudes of I_{SC} peaks at contact and separation.

Figure 4-4 Surface modification by oxidation and reduction process of metal electrode for fine porous structure. (a)Schematics of oxidation and reduction condition for the metal; (b)Microscope image and (c) Isc generated with metal electrode before treatment; (d)Microscope image and (e) Isc generated with metal electrode after treatment.

4.3.3 Surface roughness morphology using sandpaper polish

Sandpaper was used to roughen the contact surface for microstructures. A two-electrode fold-up structured device was fabricated with a 5 cm x 5 cm Al tape and PET, as shown in Figure 4-5(a). The surface of the contact electrode Al was then polished with sandpaper in arbitrary directions, followed by cleaning with deionised (DI) water and drying with nitrogen gas. The microscope images before and after polishing with

sandpaper are shown in Figure 4-5(b)(d), from which the microstructures on the surface can be confirmed. The I_{SC} generated under a contact force of 5 N for both plain and sandpaper polished Al surfaces are shown in Figure 4-5(c)(e), where the peak of I_{SC} doubled from around $0.7 \mu A$ before polishing to nearly $1.5 \mu A$ after the treatment, suggesting that to polish the contact surface with sandpaper can be a promising method in enhancing surface charge density. This treatment is not restricted to sample size.

Figure 4-5 Surface modification by polishing with sandpaper. (a) Schematics of sandpaper treatment for a TENG made in two-electrode fold-up structure with $5 \text{ cm} \times 5 \text{ cm}$ Al tape and PET film; (b) Microscope image of the Al electrode before treatment and (c) I_{SC} generated with a contact force of 5 N; (d) Microscope image of the Al contact surface after sandpaper polishing and (e) I_{SC} generated with the same contact force.

Although in most reported TENGs, the surface treatments were commonly applied for the insulator surfaces, the modifications on contact metals can be also effective and more diverse.

4.4 Influences of contact/separate frequency and external load resistance

As introduced in Section 2.3 that TENG is a pure capacitive generator which can generate AC current via changing the capacitance such as contact-separate two electrodes. The frequency f of contact-separate motions was changed from 1 Hz (such that the two surfaces periodically moved relatively and came to contact once per second) up to 14 Hz while maintaining the maximum contact force at 1 N. Figure 4-6 shows the average peak values of I_{SC} and V_{OC} at each frequency. It can be seen that the magnitude of V_{OC} maintained relatively constant while I_{SC} increased proportionally with f . By the definition that current equals to the amount of charge flows per unit time, so for TENGs working under the vertical contact-separate mode, the magnitude of I_{SC} is determined by the total charge $Q_{SC,max}$ induced with the maximum gap variation. Assume the maximum separation between the two electrodes was sufficiently large, such that the amount of induced charge could be approximated to the total surface electrostatic charge, which was determined by the average surface charge density σ and contact area S . Hence, as shown in equation (4.1), the magnitude of I_{SC} relation is linearly proportional to f .

$$|I_{SC}| = \left| \frac{dQ_{SC}}{dt} \right| = \frac{|Q_{SC,max}|}{T} \approx \frac{\sigma S}{T} = \sigma S f \quad (4.1)$$

Meanwhile, the voltage over the generator can be calculated via the capacitance variation $C(x)$ with

$$|V_{OC}| = \left| \frac{Q_{SC}}{C(x)} \right| \approx \frac{\sigma S}{\epsilon A} d \quad (4.2)$$

where ε is the effective permittivity in between the two electrodes, A is the area of the electrode and d is the maximum gap distance. Therefore, the magnitude of V_{oc} is dependent on the surface charge as well as the electrode dimension and maximum gap variation, rather than frequency.

Figure 4-6 Open-circuit voltage V_{oc} and short-circuit current I_{sc} at different frequencies for $2\text{ cm} \times 2\text{ cm}$ Al plate in contact with Kapton film under 1 N.

As the TENG device generates purely displacement current, which is restrained by the RC time in the circuit, different load resistance R was connected to the external circuit to observe the current variation. Figure 4-7(a) shows an arbitrary cycle of the instantaneous current waveform measured at 1 Hz under a contact force of 5 N. With larger R , the width of the current signal broadened, and when R was $100\text{ M}\Omega$ or above, the negative peak (approaching) ‘jumped’ to the positive peak (separating), without returning to zero, which corresponding to incomplete charging and discharging processes.

In addition, Figure 4-7(b) shows the amount of charges generated with increasing at different frequencies, and among which the longest contact duration was 70 ms (at 1 Hz). It is evidently shown that the charge generated in each cycle decay with increasing

load and/or frequency, supporting the observed incomplete charging/discharging processes as observed in Figure 4-7(a). This behaviour is due to the restraint of RC time, which is unavoidable for capacitive generators. Existing TENGs are equipped with capability in harvesting energy from low-frequency motions like human walking and water wave, but the effects from RC time limit the flexibility of integrating TENG with fast operating mechanics. Hence, alternative solutions for random energy harvesting will be necessary.

Figure 4-7 (a) One arbitrary cycle of current vs time when different load resistances were connected in the external circuit; (b) charge transferred under various load resistance at different frequencies. The two contact materials were $2 \text{ cm} \times 2 \text{ cm}$ Al plate and Kapton film with the contact force maintained at 5N.

4.5 Conclusions

In this chapter, three simple structures, including the double-electrode and multi-layer fold-up structures and the wrapped single electrode structure, consisting of a metal electrode in contact with a polymer film were designed and constructed for studying TENGs.

The device performance improvement was achieved through three surface modification approaches for surface asperity contact enhancement, including by using pressed metal

foams, by undergoing oxidation and reduction processes for refined porous structures and by polishing with sandpaper. Among the mentioned techniques, using the pressed metal foam improved 30% in the I_{SC} , while the Ni foil after the oxidation/reduction processes doubled the magnitude in I_{SC} output. By polishing the Al electrode before contacting with PET film, the magnitude of I_{SC} was more than doubled too.

The influences on the device performance were investigated by altering contact/separation frequency and load resistance. When adjusting the contact/separation frequency from 1 – 14 Hz, the averaged peak value of I_{SC} increased linearly with frequency while the V_{OC} show insignificant dependence. But when load resistance was added in the external circuit, the charge transferred under electrostatic induction reduced with higher frequency and larger load resistance due to RC time. As only displacement current is generated in TENGs, the delay from RC time is unavoidable, which could become a crucial drawback for a TENG to be integrated for higher frequency mechanical energy harvester or sensors. To mitigate this confinement, novel types of generator were developed and will be introduced in Chapter 5 and Chapter 6.

Chapter 5   One-Direction Dominated Current

Generator by Mechanical Impact on Two Doped Semiconductors

5.1 Introduction

Mechanical-electrical energy generators are one of the promising solutions in energy harvesting [150]. Typically, there are four groups of electric generators, electromagnetic, piezoelectric, electrostatic, and triboelectric generators. In an electromagnetic generator, we rotate a wire coil in a magnetic field to generate an electromotive force that drives electrons to flow in the coil and external circuit based on Faraday's law [3]. Depends on if the magnetic flux passing through the coil increases or decreases, the resultant current turns to be negative or positive alternatively. In a complete cycle, the amount of charges under negative current will be the same as that flow under positive current. Piezoelectric generators make use of piezoelectric materials, so that the material will be polarised along certain orientation under a tension or compression strain, leading to a potential difference over the terminals [151]–[153]. As most of piezoelectric materials are of high electrical resistivity, the induced charges will not flow across the material. Instead, the potential difference is balanced by inducing electrons and discharge them off once strain is released. Electrostatic generators and triboelectric generators generate electricity under capacitive coupling, such that by modulating the capacitance between the two electrodes, generally via relative motion, the electrostatic electric field varies, resulting in charges flow in the external circuit back and forth under electrostatic induction. The initialisation of charges can be achieved through triboelectric effect [105], [154], [155], electrostatic induction

[156]–[159] or simply from the chemical potential difference of the electrodes [160], [161].

When look at the four groups, electromagnetic generators produce conduction current only, where the current is due to the flow of electrons flow in the coil. The internal resistance is low, but it is very challenging to achieve miniaturisation [162]–[166]. As for the rest three, they can only generate displacement current under capacitive coupling, where the current is due to displacement of electrons in a time-varying electric field. Thus, electrons move from one electrode to the other through whole external load, which leads to their large internal impedance, restraining power delivery efficiency especially under high-frequency applications. Moreover, all the four types of generators generate AC, and without any rectification, the amount of charge transferred in the positive current equal to that generated in the negative part for a full cycle. In other words, there is not net charge flow in either direction for all these four generators.

In this chapter, a novel type of generators based on mechanical impact of p-n junctions is developed. With intermittent contact/separate motions, one-direction dominated current can be generated. With this one generator, both displacement current and conduction current are generated, converting mechanical energy to electrical energy.

5.2 Experiment methodologies

5.2.1 Electrodes preparation

Doped silicon (Si) wafers were used as electrodes, including heavily boron doped p-type Si (resistivity $\rho \sim 10^{-3} \Omega \cdot \text{cm}$, doping concentration $N_A \sim 2 \times 10^{19} \text{ cm}^{-3}$), lightly boron doped p-type Si ($\rho \sim 5 \Omega \cdot \text{cm}$, $N_A \sim 3 \times 10^{15} \text{ cm}^{-3}$), heavily phosphorus doped n-type Si ($\rho \sim 10^{-3} \Omega \cdot \text{cm}$, doping concentration $N_D \sim 10^{19} \text{ cm}^{-3}$) and lightly phosphorus doped n-type Si ($\rho \sim 5 \Omega \cdot \text{cm}$, $N_D \sim 10^{15} \text{ cm}^{-3}$). The electrodes were in a dimension of

$2.0 \times 2.0 \text{ cm}^2$, and they were cleaned in an ultrasonic tank with acetone, isopropyl alcohol (IPA) and deionised (DI) water for 8 minutes sequentially, followed by dipping in 1:10 diluted hydrofluoric acid (HF) (49%) for 1 minute to etch away the native oxide layers. For n-type Si, a 10-nm Ti /100-nm Au contact pad was deposited on the non-polished side (backside) using e-beam evaporator; for p-type Si, a 10-nm Al / 100-nm Au contact pad was deposited. The samples were then annealed in Argon at 400 °C for 30 minutes for ohmic contact. The electrode contact performance was confirmed using a semiconductor analyser (Keithley 4200SCS) as shown in Figure 5-1. The as-fabricated Si samples were then directly used as the electrodes by wiring out from the deposited metal pads.

Figure 5-1 Ohmic contact of back electrode for (a) n-type and (b) p-type Si electrodes.

Alternative electrodes using heavily zinc doped p-type gallium arsenide (GaAs) and heavily silicon doped n-type GaAs were also fabricated. GaAs wafers were cleaned with acetone, IPA and DI water sequentially, followed by dipping in 1:10 diluted HCl solution for 30 seconds to etch away native oxide layers. For p-type GaAs, a 10-nm Ti /100-nm Au contact pad was deposited on the non-polished side; for n-type GaAs, a five-layer contact pad of Ni /Ge /Au /Ni /Au (5 nm/20 nm/ 100 nm/20 nm/100 nm) was deposited using electron beam evaporation. After the deposition, the electrodes were annealed in rapid thermal process (RTP) at 380 °C for 30 seconds.

Insulating electrodes were fabricated by depositing a 100-nm SiO₂ layer on the heavily doped p-type Si using sputtering.

All the electrodes were kept in a vacuum box with N₂ before and after the experiments to reduce contamination and oxidation. Dimensions of 0.5 cm × 0.5 cm, 1.0 cm × 1.0 cm, 1.5 cm × 1.5 cm and 2.0 cm × 2.0 cm of electrodes have been prepared.

5.2.2 Measurement setups for contact-separation motion cycles

The n-type Si was fixed on the translation stage of a linear motor (LinMot E1100-GP), and the p-type Si was fixed on a stationary sample holder behind which a force gauge was installed. The distance between the two electrodes was varied from contacting to a gap of $d = 2.5$ mm. The two electrodes contacted at a frequency of around 0.5 Hz, the duration of contact was set to be 1 second and the contact force was controlled to be 5 N.

The two electrodes were connected through the external circuit with a current pre-amplifier (SRS 570) and an adjustable resistor in series, and a voltage pre-amplifier (SRS 560) was connected in parallel with the resistor. The capacitance of two electrodes in contact was measured using Keithley 420SCS by sweeping a bias voltage from -0.2 V to $+0.2$ V. The potential difference was measured using the variable capacitance method, where a voltage source (Keithley 2400) was swept from -1 V to 1 V at a step of 10 mV while the two electrodes vibrating at a frequency of 2 Hz. The potential difference was determined at the bias giving the minimum current.

5.3 The working principles

Figure 5-2(a) shows a photo when the two electrodes are mounted and disconnected, and their energy band diagrams are shown in Figure 5-2(b). For a p-type Si, it possesses

a larger work function than an n-type Si, such that when the two electrodes are disconnected, the Fermi level of p-type lies lower than that of the n-type.

Figure 5-2 (a) A photo of a pair of Si electrodes mounted on to the sample holders; (b) the energy band diagram when the two Si electrodes are disconnected. E_0 the vacuum level, E_F the Fermi level, E_V the top of valence band E_C the bottom of conduction band, and $q\phi$ the work function.

When the two electrodes are contacted intimately (Figure 5-3(a)), free electrons diffuse from n-type to p-type, and holes from p-type to n-type, leaving positively charged region in n-side and negatively charged region in p-side. The charged space regions form a built-in electric field that hinders the diffusion process, such that at thermal equilibrium, there is no net current flow either across the region or in the external circuit, and the Fermi levels of the two electrodes align. At thermal equilibrium, the p-n junction is formed. The space charge region within the p-type has a width of W_p and that within the n-type is W_n . A built-in voltage V_{bi} equals the potential difference $|\phi_1 - \phi_2|$ is then dropped across the whole depletion region with a total width of $W = W_p + W_n$. As the electron exchange happens at the interface, there is no transient current in the external circuit. Once the two electrodes are separated with a tiny gap (Figure 5-3(b)), V_{bi} drops partially over the air gap, resulting in narrowing of the space charge regions in both electrodes with new widths of w_p and w_n respectively. The excess electrons previously

in the region are then discharged through the external circuit, generating a transient current flow from the n-type to the p-type electrode through external load. When the electrodes are fully separated with the furthest distance d_f and stop (Figure 5-3(c)), they reach to another thermal equilibrium, and there will be no more transient current in the circuit. During this separation motion, a transient current is generated at the stage of separating (Figure 5-3 The energy band diagrams and space charge distribution for contacting and separating a pair of p-type and n-type semiconductor electrodes when they are (a) contacted; (b) during separating; (c) separated with a maximum distance of d_f ; (d) during approaching, and (e) during contacting.), which is corresponding to the discharge of space charges. This current is a displacement current, and the amount of charge transferred in this current should equal to that in the space charge region formed previously.

In the next stage of approaching (Figure 5-3(d)), because of the chemical potential difference, the space charge region is gradually restored through electrostatic induction when the gap is reducing. This process results in another transient current flowing in the opposite direction through the external circuit. However, when two electrodes are contacting (Figure 5-3(e)), because the electrodes are semiconductors, electrons and holes can then diffuse across the contact surfaces. As the transient current during approaching is resisted by external load, the space charge region may not be completely replenished. As a result, the remaining charges will diffuse across the contact surfaces at the very moment of contact, accomplished by re-establishment of the built-in electric field. This is the process for space charge restoration under electron diffusion. After the diffusion process, the electrodes then quickly reach back to thermal equilibrium where the p-n junction is formed (Figure 5-3(a)). Typically, the duration for this diffusion can be estimated via the drift time for electrons in forming the p-n junction, which is in the range of 0.1 ns [167]. As this process happens at the interface, no significant transient

current can be detected in the external circuit. During the whole contact motion, the transient current due to electrostatic induction at approaching stage is displacement current, whereas the electron flow across the contact surfaces is conduction current. Furthermore, the total amount of charge transferred under the two processes should equal to that in the space charge region, which also equals to the amount of charges pumped out during previous separation.

Unlike conventional electrostatic generators that electrons only flow through external loads under electrostatic induction, which is necessarily affected by RC time in the circuit, our generator involves charge restoration via diffusion, avoiding RC delay and promoting a one-direction dominated current generation. Both displacement current and conduction current are created in this generator.

Figure 5-3 The energy band diagrams and space charge distribution for contacting and separating a pair of p-type and n-type semiconductor electrodes when they are (a)

contacted; (b) during separating; (c) separated with a maximum distance of d_f ; (d) during approaching, and (e) during contacting.

5.4 Results and discussions

5.4.1 Mechanical energy to electrical energy conversion with one-direction dominated current flow

A highly doped p-type silicon was connected with a lightly doped n-type silicon electrode through external loads, with the current meter and an adjustable load resistance R connected in series. A voltage meter was connected in parallel to R . Figure 5-4 shows two arbitrary cycles of the transient current i and voltage v over R measured with respect to the gap distance d when $R = 50 \text{ M}\Omega$ was used. Starting with two electrodes already in contact (Stage A, corresponding to Figure 5-3(a)), no current was generated in the external circuit. While the electrodes were separated gradually (Stage B, corresponding to Figure 5-3(b)), a transient current was observed flowing from n-type electrode to p-type. This current quickly dropped to zero as soon as the separation stopped at the maximum gap distance d_f of 2.5 mm (Stage C, corresponding to Figure 5-3(c)). When the electrodes were moved to close again (Stage D, corresponding to Figure 5-3(d)), a current was detected flowing from p-type to n-type in the external circuit. At the moment the two electrodes were in contact again (Stage A, corresponding to Figure 5-3(e) & (a)), the current flowing in the external circuit immediately dropped to zero. The peak generated at Stage B was significantly larger than that generated at Stage D, showing a one-direction dominated current.

Figure 5-4 The instantaneous gap distance d (upper), voltage v over a $50\text{ M}\Omega$ load resistance (middle) and transient current i (lower) by contacting and separating a pair of p^+ - n -type Si electrodes. [167]

The current generation is consistent with the mechanism discussed in Section 5.3. The depletion region (or p - n junction) formation was confirmed by measuring the current rectification characteristic curve (or called IV curve) using a semiconductor analyser (Agilent B1500), shown in Figure 5-5(a). The IV curve was measured when a heavily doped p -type silicon was in contact with a lightly doped n -type silicon electrode under a contact force of 5 N. Meanwhile, the IV curves with two same n -type silicon electrodes (Figure 5-5(b)) and two p -type silicon electrodes (Figure 5-5(c)) in contact were measured. In both cases, the IV curves showed ohmic-like behaviour, which further confirmed that the rectification in Figure 5-5(a) was truly due to p - n junction formed at contact.

Figure 5-5 The current rectification characteristic curve I under sweeping a voltage bias V when (a) p-type and n-type (b) n-type and n-type (c) p-type and p-type electrodes were in contact under a force of 5 N.

The work function difference was determined using the variable capacitance method, the mechanism is illustrated in Figure 5-6. When two semiconducting/metallic electrodes with different work functions are connected, their Fermi levels should be aligned under thermal equilibrium, resulting in a built-in voltage [161]. This potential difference thus induces opposite charges accumulated in the two electrodes, which is an analogy to a capacitor. When the gap between the two electrodes is varied, the capacitance varies and hence electrons flow back and forth to balance the potential difference. When a voltage bias is applied against the built-in voltage, the net electric field can be partially cancelled and fewer charges are induced in the electrodes, generating smaller currents when the two electrodes are vibrated. The current reaches the minima when the magnitude of the bias voltage is the same as the built-in voltage, and the direction of charge flow reverses when the bias is further increased. Based on this principle, the voltage bias at which zero current was generated under vibration is the built-in voltage formed between the electrodes. Figure 5-7 shows the current measured with respect to the voltage bias while vibrating two p- and n-type Si electrodes. The current reached to a minimum when the biased voltage was -0.28 V, suggesting the built-in voltage of these two electrodes was around 0.28 V.

Figure 5-6 Mechanism of variable capacitance method to determine V_{bi} . Energy band diagram when two electrodes are (a) isolated; (b) connected and (c) when a bias voltage is applied over the electrodes.

Figure 5-7 Determination of V_{bi} of a pair of p⁺-n Si electrodes. [167]

As discussed earlier, this generator can only displacement current is generated during separation but both displacement current and conduction current during contact process. Known that displacement current is resisted by external circuit but not for conduction current, modulating the resistance in external circuit can lead to difference for both separation and contact processes. Figure 5-8(a) shows the current measured during a single cycle of contact/separate with different load resistances R connected. Negative pulse currents were detected when the two electrodes were just separated, while positive pulses were detected right before they were contacted. Furthermore, the magnitudes of

the charge discharged at separation $Q_{\text{int-neg}}$ and the charge charged at contact $Q_{\text{int-pos}}$ under different loads are shown in Figure 5-8(b). They were calculated from $|Q_{\text{int-neg}}| = \int_0^{t_{\text{-neg}}} i dt$ and $|Q_{\text{int-pos}}| = \int_0^{t_{\text{-pos}}} i dt$ respectively, where t_{neg} (t_{pos}) is the time duration of the negative (positive) pulse current.

Figure 5-8 (a) The transient current i and (b) the amount of charge transferred in the external circuit by separating and contacting a pair of Si electrodes with variable R . [167]

When R was smaller than 1 M Ω , the magnitudes of both negative and positive pulses were comparable. Similar for the charges transferred under the separation peak and contact peak. This is because that when R is small, the resistance for electrons to flow under electrostatic induction is low, so that most of the space charges can be restored just within approaching stage. However, when R was gradually increased, the reduction in the magnitude for the positive pulses were observed to be more prominent than the negative ones. For example, for R increased from 1 M to 10 M, the peak values of the positive pulses decreased from 1.19 nA to 0.56 nA, while that for the negative pulses only decreased from 2.22 to 2.17 nA. Also, for the integrated charges, with increasing R , $Q_{\text{int-pos}}$ decreased significantly while $Q_{\text{int-neg}}$ remained constant, resulting in larger difference in charges transferred during the two processes. For instance, at short circuit, the charge difference in one motion cycle $\Delta Q_{\text{int}} (= Q_{\text{int-neg}} - Q_{\text{int-pos}})$ was around 7 pC,

and the ratio $Q_{\text{int-neg}} / Q_{\text{int-pos}} \sim 1.1$. However, ΔQ_{int} gradually increased when the load increased, and at $R = 1 \text{ G}\Omega$, ΔQ_{int} was around 60 pC with $Q_{\text{int-neg}} / Q_{\text{int-pos}} \sim 50$, showing a one-direction dominated charge transfer. This is because, when R increases, electrons flowing under electrostatic induction slows down. However, at separation, the space charges can only be discharged through external circuit, generating a transient current with the amount of charge equal to that of the space charges. Whereas for contact, the space charge region cannot be replenished within approaching stage, and the remaining is accomplished by electrons diffusing when two electrodes contacting. Based on charge conservation, ΔQ_{int} should equal to the part of the electrons that had been transferred across the interface via diffusion.

Figure 5-9 Average power delivered to increasing R by positive pulses (at contact) and negative pulses (at separation) respectively. [167]

The average peak power $\bar{P}$ dissipated on the loads R from the negative and positive pulses respectively are shown in Figure 5-9, calculated from $\bar{P} = R \int_0^{t_s} i^2 dt / t_s$, where t_s is the duration of the pulse current. Overall, the negative pulses (at separation) delivered more average power than the positive pulses (at contact). When R was around 20 M Ω , a maximum $\bar{P}$ of 2.7 pW was delivered to the load from the positive pulse,

whereas $\bar{P}$ delivered by the negative pulse was 24.5 pW. When R was increased to 100 M Ω , $\bar{P}$ from the positive pulse dropped to 0.92 pW while that from the negative pulse further increased to 29.9 pW, dominating power dissipation. This characteristic differs this system from all traditional electrostatic generators, where the amount of charges transferred during charging and discharging processes are comparable.

In two control experiments, where the diffusion process was prohibited, such as by depositing a thin layer of insulator between the contact surfaces or approaching closely but still with a tiny gap, the difference of charge transfer when varying the load resistance was not observed. Figure 5-10 show the output from a pair of Si electrodes, where a 100-nm thin layer of SiO₂ was coated to the surface on the p-type Si electrode while the n-type Si electrode was unchanged. The contact force between two electrodes was fixed as 5 N, and the maximum separation distance was 2.5 mm. Figure 5-10(a) shows the transient current and the voltage measured over a 50 M Ω load resistance and Figure 5-10(b) shows the charges detected at contact and at separation under different load resistances. AC currents with comparable peak values were observed at contact and at separation for all R used, due to the fact that the chemical potential of the SiO₂ layer was higher than n-type Si surface, the polarity of current reversed from the pure p-n electrodes. The magnitudes for $Q_{\text{int-neg}}$ and $Q_{\text{int-pos}}$ fluctuated slightly with different R , but ΔQ_{int} was always around zero and was independent of R . Similarly, in another experiment, the p-type and n-type Si electrodes were approached without really contact, such that there was still a tiny gap distance of 0.5 mm at the closest point. The current output and charge transfer are shown in Figure 5-11, showing negligible difference in charge transfer for all R . Both experiments well convinced that the ΔQ_{int} originated from the electrons transfer across the interface.

Figure 5-10 (a) Transient current and voltage output with a 50 M Ω resistor connected; (b) magnitudes of charge generated at positive and negative pulse currents. Electrodes: 100-nm SiO₂ coated on p-type Si vs n-type Si;

Figure 5-11 (a) Transient current and voltage output with a 50 M Ω resistor connected for approaching with 0.5 mm air gap; (b) magnitudes of charge generated at positive and negative pulse currents. Electrodes: p-type Si vs n-type Si;

5.4.2 Theoretical calculation for charge generation

The amount of charges detected in the circuit is associated with the space charge region. The theoretical value of total charge in the region can be estimated with the charge distribution within the p-n junction, illustrated as in Figure 5-12. Figure 5-12(a) shows the charge distribution of an ideal abrupt p-n junction, where the p-type semiconductor has an acceptor concentration of N_A and the n-type semiconductor has a donor concentration of N_D . At thermal equilibrium, free carriers are depleted with a width of

W_p extended into the p-type side and W_n into the n-type side, and the charge distribution can be expressed as

$$\rho(x) = \begin{cases} -qN_A, & \text{for } -W_p \leq x \leq 0 \\ +qN_D, & \text{for } 0 \leq x \leq W_n \end{cases} \quad (5.1)$$

For an ideal p-n junction, the built-in voltage V_{bi} is formed over the depletion region and can be expressed as [119]

$$V_{bi} = \frac{qN_D W_n^2}{2\epsilon_0 \epsilon_r} + \frac{qN_A W_p^2}{2\epsilon_0 \epsilon_r} \quad (5.2)$$

where ϵ_0 is the permittivity of free space. ϵ_r is the dielectric constant of the semiconductor. Owing to the overall charge neutrality, the total negative charge in the p-side should equal to the positive charge in the n-side. Thus, the total space charge in the depletion region is $Q_S = qN_D W_n = qN_A W_p$. Hence, the built-in voltage V_{bi} can be reformed to be

$$V_{bi} = \frac{Q_S(W_n + W_p)}{2\epsilon_0 \epsilon_r} \quad (5.3)$$

V_{bi} can be regarded as the voltage over the electrodes of a capacitor containing a charge amount of Q_S , and when the p-type and n-type electrodes are intimately contacted, V_{bi} is fully dropped over the two depletion regions with the width of $W = W_n + W_p$.

When the two electrodes are separated with a gap, the junction is then disturbed, and the space charge redistributes in both p-type and n-type electrodes as shown in Figure 5-12(b). With the final separation of d_f , the new space charge distribution can be expressed to be

$$\rho(x) = \begin{cases} -qN_A, & \text{for } -w_p \leq x \leq 0 \\ 0, & \text{for } 0 \leq x \leq d_f \\ +qN_D, & \text{for } d_f \leq x \leq w_n + d_f \end{cases} \quad (5.4)$$

where w_p and w_n are the new depletion widths in the p-side and n-side respectively. Comparing to the contacted stage, there is an additional capacitor introduced in series between the original depletion regions, dividing V_{bi} . The V_{bi} becomes:

$$V_{bi} = \frac{qN_D w_n^2}{2\varepsilon_0 \varepsilon_r} + \frac{qN_A w_p^2}{2\varepsilon_0 \varepsilon_r} + \frac{qN_D w_n d_f}{\varepsilon_0} \quad (5.5)$$

With the space charge neutrality, V_{bi} can be expressed into

$$V_{bi} = \frac{Q'_S(w_n + w_p)}{2\varepsilon_0 \varepsilon_r} + \frac{Q'_S d_f}{\varepsilon_0} \quad (5.6)$$

where the remaining space charge $Q'_S = qN_D w_n = qN_A w_p$. As the V_{bi} is essentially determined by the difference in Fermi-level energy of p- and n-type semiconductors via $V_{bi} = \frac{kT}{q} \ln \left(\frac{N_A N_D}{n_i^2} \right)$ [119], where T is the temperature in Kelvin, n_i is the intrinsic carrier concentration, the depletion region must shrink and charges are pumped out to the circuit during the electrode separation. The amount of the charge can be estimated as

$$\Delta Q = Q_S - Q'_S = Q_S \left(1 - \frac{w_n + w_p}{w_n + w_p + 2\varepsilon_r d_f} \right) = Q_S \left(1 - \frac{w}{w + 2\varepsilon_r d_f} \right) \quad (5.7)$$

with $w = w_n + w_p$. When the two electrodes are separated with a gap width comparable to the total width of the space charge region formed during the contacted stage, most of the diffused charges can be extracted at separation. With conditions used for the experiment results discussed above, i.e., $N_A \sim 5 \times 10^{19} \text{ cm}^{-3}$, $N_D \sim 2 \times 10^{15} \text{ cm}^{-3}$, $T = 300 \text{ K}$ and $n_i = 1.5 \times 10^{10} \text{ cm}^{-3}$, V_{bi} is calculated to be $\sim 0.9 \text{ V}$. Since $N_A W_p = N_D W_n$, the depletion region mainly exists in n-type electrode with $W \approx W_n = \sqrt{\frac{2\varepsilon_0 \varepsilon_r V_{bi}}{q} \cdot \frac{N_A}{N_D(N_A + N_D)}} \sim 0.8 \mu\text{m} \gg W_p$. By separating with a distance of 2.5 mm, the space charges can be estimated to be discharged almost entirely with $Q_S = qN_D W_n \sim 1 \times 10^{-7} \text{ C}$. However, the experimental result of charges pumped out at

separation $Q_{\text{int-neg}}$ was only 6×10^{-11} C, which was nearly 3 orders less than the theoretical value. This huge difference is because of the assumption of the ideal contact surfaces. In fact, for silicon and other semiconductors, the surface states exist and will negatively affect the output. The details of nonideal surfaces will be further discussed in Section 5.4.3.

Figure 5-12 Space charge distributions of two semiconductor electrodes (a) when in contact with depletion widths of W_n in n-type side and W_p in p-type side; and (b) when separated with a gap of d_f , the new depletion widths are w_n in n-type side and w_p in p-type side respectively. N_D and N_A are the donor concentration and acceptor concentration respectively. [167]

5.4.3 Influences of nonideal surface contact in charge generation

For any semiconductors, due to the termination of lattice periodicity at the surface, a high surface density of dangling bonds with unpaired electrons may exist, they interact with each other and form electronic states within the semiconductor bandgap [168]. Those states accommodate electrons or holes, result in different charge distribution near the surface, and exhibit differently from the bulk material. The Fermi level on the

surface usually bends to the equilibrium, or called Fermi level pinning [168]–[170], and a high density of surface states may even screen the influence of the bulk, leading to an additional modification to the electron affinity at the surface [171].

Several techniques can estimate the surface states via measuring the band bending at the semiconductor surfaces with Photoelectron Spectroscopy (PES), Photoluminescence (PL) Spectroscopy, Surface Photovoltage (SPV) Measurements, Scanning Probe Microscopy (SPM), etc. [172] It is suggested that the contact-induced band bending of the covalent semiconductors (Si, GaAs, etc.) are usually less dependent on the bulk than the ionic semiconductors (ZnO, TiO₂, etc.) because of the higher density of surface states in their band gaps [173]. Also, on the same semiconductor, the surface states will be determined by the atomic structure or crystalline orientation.

The native oxide layer on Si electrodes also causes non-ideal contact. When the two surfaces are contacted, the ultra-thin insulating SiO₂ in the middle shares most of the built-in voltage and hence slow down the electron diffusion, which results in shallower depletion width.

Although the surface states cannot be eliminated, they can be moderated through proper surface treatment [174]. In our approach, the silicon electrodes were dipped in diluted HF solution for 1 min to etch away the native oxide layers and contaminants and finish the Si surface with H-terminated. The mechanism of HF treatment is shown in Figure 5-13.

Figure 5-13 Schematic representation of the mechanism of H passivation of Si surfaces dipped in HF solution [175]

As the Si – F bonds are more stable than Si – O bonds, HF can be used to remove the oxides and terminate the Si dangling bonds with F. While within the newly formed Si—F bonds, electrons transfer from Si to F and form an electrostatic reinforcement, which induces polarization in the Si-Si backbonds where HF can then insert into. Thus, the F of the next H – F will be bonded to the top layer of Si while the H will be bonded to the bottom layer of Si. With sufficient HF, the top layer of Si will be fully bonded with F and separated from the bulk in the form of SiF₄, leaving bottom layer to become the fresh surface and terminated with H [175].

The comparison of I-V characteristic curves and the output of the same device are shown in Figure 5-14 and Figure 5-15. After the surface treatment by dipping in HF solution, the formation of the p-n junction of the two contacted surfaces between p⁺-type and n-type silicon electrodes as well as the pumped charges were found to be significantly improved. Particularly, the charge generated from the contact did not show significant improvement before or after the HF treatment, but that generated at the separation was boosted from around 35 pC to 55 pC after dipping in HF, which indicates that more electrons were able to diffuse across the interface possibly due to thinner oxide layer and relaxed surface defects. However, this improvement cannot maintain for a long time.

The improved outputs were observed to decay over time since the H-terminated surface can be easily re-oxidized or re-contaminate in the ambient environment.

Figure 5-14 The influence of HF treatment on the I-V characteristic for p-n junction formed by p^+ -Si and n-Si electrodes in contact.

Figure 5-15 The influence of HF treatment on the transient current and charge. (a) The transient current from the p^+ -Si and n-Si electrode pair with 50 M Ω load resistance connected; and (b) the integrated charge with increasing R.

In general, the actual surfaces of the electrodes can be influenced by the surface states, surface potential barrier, the Fermi level pinning, the native oxide layer, imperfect contact, etc. All these factors make the surface contact nonideal, which can even change the electronic properties of a semiconductor electrode, and extensively suppress the amount of charges extracted out. In order to significantly improve the performance of

the devices, a possible approach is to reduce the influence of surface states. One possible method to remove these surface states is to saturate the dangling bonds by adatoms and replace them by adsorbate-induced states with H terminated.

5.4.4 Influence of contact/separation frequency

The RC time restriction was studied for this generator via frequency response. As the space charges region can be restored through diffusion when two surfaces are contacted, rather than the solo mechanism via electrostatic induction in TENGs, the one-direction current generation characteristic should be more prominent when RC time in the circuit is large. Besides increasing R in the circuit, the impact frequency was increased from 1 Hz to 10 Hz to study the charge transfer.

A small impact system shown in Figure 5-16 Photograph of the small impact system. was used to contact and separate two electrodes at frequencies from 1 Hz to 10 Hz. This system was driven by an eccentric circle on the left that rotates and pushes the arm of the translation stage back and forth towards a stationary sample holder on the right. By controlling the angular speed of the eccentric circle, the frequencies of contacting/separating could be modified accordingly. At contact, a dynamic contact force between two holders varies according to the Hooke's law, raised from the deformation of the buffer spring behind the translation stage. At the back of the fixed sample holder, a force gauge with a sensitivity of 0.01 N was installed.

Figure 5-16 Photograph of the small impact system.

With maintaining the maximum contact force of 5 N, the frequency was adjusted from 1 Hz to 10 Hz, and at each frequency, the current in the external circuit was measured while increasing the load resistance from around 0 Ω (short-circuit) to 1 G Ω gradually. The amount of charge was calculated via integration of the current with respect to time.

Figure 5-17 Integrated charge for the positive transient current contact and the negative current at separation as a function of the load resistance R at (a) 1 Hz, (b) 3 Hz, (c) 5 Hz, (d) 7 Hz, (e) 8 Hz and (f) 10 Hz respectively. (Electrodes: 2 cm $\times$ 2 cm sized p⁺-type Si vs n-type Si. Maximum contact force: 5 N).. show $|Q_{\text{int-pos}}|$ and $|Q_{\text{int-neg}}|$ with R increased from 100k Ω to 100 M Ω at difference frequencies. It was observed that for each cycle of contact/separate, ΔQ increased with larger R at all frequencies. As explained before that the charge obtained at separation should be comparable to the available space charges in the junction. Although RC time in the circuit impedes the space charge restoration via electrostatic induction, the charges are still able to be replenished via diffusion once in contact, therefore the compliance of space charge region is not significantly affected by RC time. However, when frequency is higher, the duration for separation also reduces, which potentially leads to incomplete discharge of the space charges, showing slightly drop for charge pumped to the external circuit at each separation for higher

frequencies. As a result, shown in Figure 5-18 The net charge generated under different frequencies and loads (a) in one single cycle $\Delta Q_{\text{per cycle}}$ and (b) within one second ΔQ_{1s} (Electrodes: 2 cm $\times$ 2 cm sized p⁺-type Si vs n-type Si. Maximum contact force: 5 N). (a), the net charge generated per contact-separate cycle $\Delta Q_{\text{per cycle}}$ appeared to be co-affected by the frequency and R, such that $\Delta Q_{\text{per cycle}}$ increased with frequency only when $R \leq 10 \text{ M}\Omega$, but it started to decrease when R was increased to 100 M Ω for frequency higher than 5 Hz. This reduction can be compensated at higher frequencies with more cycles completed within the same time for pumping. Shown in Figure 5-18(b), the average net charge obtained during one second ΔQ_{1s} increased with increasing frequency and R. Furthermore, the one-direction charge transfer characteristic can be realised even with a smaller R at higher frequency.

Figure 5-17 Integrated charge for the positive transient current contact and the negative current at separation as a function of the load resistance R at (a) 1 Hz, (b) 3 Hz, (c) 5 Hz, (d) 7 Hz, (e) 8 Hz and (f) 10 Hz respectively. (Electrodes: 2 cm $\times$ 2 cm sized p^+ -type Si vs n -type Si. Maximum contact force: 5 N).

Figure 5-18 The net charge generated under different frequencies and loads (a) in one single cycle $\Delta Q_{\text{per cycle}}$ and (b) within one second ΔQ_{1s} (Electrodes: 2 cm $\times$ 2 cm sized p⁺-type Si vs n-type Si. Maximum contact force: 5 N).

5.4.5 Influence of electrode sizes and materials

Electrodes with different contact areas were used, including 0.5 cm $\times$ 0.5 cm, 1.0 cm $\times$ 1.0 cm, 1.5 cm $\times$ 1.5 cm and 2.0 cm $\times$ 2.0 cm. Same phenomena were observed, such that with increasing load resistance, the charge detected at separation maintained constant while that during contact reduced. Figure 5-19(a) shows the transient currents detected and Figure 5-19(b) shows the charge calculated for all four sizes with 50 MΩ connected. With the same apparent contact pressure (10 kPa), the charge detected at both contact and separation increased almost linearly with the areas. Also, a greater difference between $|Q_{\text{int-neg}}|$ and $|Q_{\text{int-pos}}|$ was obtained for larger sized electrodes, clearly due to the increased amount of electrons had diffused across the interface.

Figure 5-19 Comparisons in (a) transient current and (b) integrated charges at separation and contact for p⁺-n Si electrode pairs with different sizes and 50 M Ω load.

The experiments were repeated for Si electrodes with different doping concentrations, GaAs electrodes and even metals. Figure 5-20 summarise the charges detected at separation and contact at 5 N respectively for several pairs of 2 cm $\times$ 2 cm sized electrodes at 0.5 Hz. As long as a non-zero V_{bi} was measured, all the electrode pairs showed phenomena as discussed above, suggesting that electrons could directly diffuse from the higher to the lower chemical potential electrode once they are brought into contact and then pumped out at separation, converting mechanical energy to electrical energy.

Figure 5-20 Charge transfer for different electrode pairs. (a) Lightly doped p-type Si and lightly doped n-type Si. (b) Heavily doped p-type S and heavily doped n-type Si. (c) n-type GaAs and p-type Si. (d) Au surface and heavily doped Si.

5.5 Conclusions

In this chapter, a type of novel electric generators was presented. By bringing a pair of oppositely doped semiconducting electrodes into contact, electrons diffuse from the electrode with higher chemical potential into the lower one, forming space charge regions. The space charges are subsequently pumped out to the external circuit when the two electrodes are separated. The contact-separate motion achieves mechanical to electrical energy conversion, generating both conduction current and displacement current. Particularly, in the approaching stage, the space charge regions in the electrode could be restored through the electrostatic induction due to the chemical potential difference; while at the contact, the charge restoration accomplished via electron

diffusion across the contact surface. The former process is common for all conventional electrostatic generators and is restrained by the RC time of the circuit; the later one is less affected.

As doped semiconductors are directly employed as the electrodes, this generator can be seamlessly integrated with other semiconductor devices, serving as a power source or mechanical sensing units. Indeed, there are still many challenges and problems such as surface states and surface contaminations, by finding solutions to reduce the effects from non-ideal contact, more charges could be output from this generator. The influences of load resistance, frequency, non-ideal surface and electrode size are discussed. Due to the dual mechanism for space charge restoration and discharging, the one-direction dominated current can be enhanced when the intermittent contact/separate frequency is increased, suggesting a promising potential in high-frequency applications.

Chapter 6   Triboelectric Cell - A Direct-Current Generator by Sliding Two Doped Semiconductors

6.1   Introduction

As introduced in Chapter 4, TENGs are well-known for their capability of harvesting mechanical energy through triboelectric effect and electrostatic induction. The charges are accumulated on the contacting material surfaces after triboelectrification, and the capacitance was altered by either varying the gap distance of two electrode surfaces or sliding two electrode surfaces to each other, generating an AC current. However, in terms of the efficiency of utilising in non-interrupted electronics, signal processing and electricity storage, direct current is more favourable. A couple of methods including structural design and circuit configuration were applied to convert AC to DC. Yang et al. [176] reported a wheel-belt structure consisting of a rubber belt and two rotatable wheels with distinct electron affinities, the belt transfer triboelectric charges with opposite polarities to the two wheels correspondingly. The triboelectric charges accumulated on the wheels and built up an electric field between them, so that an electrical breakdown of air happened, generating a DC current in the external load. Rectification with full-wave bridge diodes [177] is also common, but the low conversion efficiency is never avoidable. Some generators are reported to regulate electron motion more favourable toward one direction and hence result in a DC output without using external rectifications. Several works reported on the Schottky contacts involving piezoelectric materials [178]–[180] or conducting polymers [181]–[183] are able to generate DC output when compression strain is applied. Wang et al. [178] reported a DC generator by using an array of aligned ZnO nanowires in contact with a Pt electrode, such that Schottky junction was formed. As ZnO nanowires induce piezoelectric

potential when under strain, when the device was exposed to ultrasonic vibration, the ZnO nanowires deflected and induced piezoelectric potential across the nanowires. While the tensile strain in ZnO induced a positive piezoelectric potential that increases the Schottky barrier and blocks current, compressive strain induced a negative piezoelectric potential that lowers the Schottky barrier and increases current flow, resulting in DC current generated in the external circuit. Shao et al. [182] reported a DC mechanical-to-electricity generator by compressing a conducting polymer (e.g. Ppy) and a semiconducting metal oxide (e.g. SnO_2) that form a non-ohmic contact at the interface. Furthermore, based on the sliding mode of TENG, DC current was generated when electrostatic breakdown happens between two charged electrode surfaces happens [146]. Liu et al. [184], [185] observed DC outputs when sliding a platinum-coated silicon AFM tip on a $\text{MoS}_2/\text{Ag}/\text{SiO}_2/\text{Si}$ substrate, which were explained as that electrons are generated at the contact surfaces by friction, and thereafter tunnel through the ultrathin insulating layer across the contacted Schottky junction, resulting in one direction current flow. Similar result was found by Lin et al. [186], i.e., a DC output was observed while sliding a metal tip on Si substrate or graphene layer. The current generation was claimed due to the dynamic appearance and disappearance of the depletion layer in the contacted Schottky junction, where the drifted electrons and holes are separated and flow back.

In this chapter, a novel electric generator, we name it triboelectric cell, is introduced. Based on the sliding friction power and built-in electric field in semiconductor junctions, a DC current is generated. The current follows the direction of the built-in electric field in the dynamic p-n junction: flowing from the p-semiconductor through the external circuit to the n-semiconductor. Different from the intermittent mechanical impact generator introduced in Chapter 5, the triboelectric cell involves dynamic processes

where the front and back of the contact region involve reformation and destroy of junctions along the movement.

6.2 Experimental methodologies

6.2.1 Electrodes preparation

Heavily boron doped p-type silicon ($\rho \sim 5 \times 10^{-3} \text{ } \Omega \cdot \text{cm}$, $N_A \sim 2 \times 10^{19} \text{ cm}^{-3}$) was used as the substrate electrode; phosphorus doped n-type silicon wafer ($\rho \sim 5 \text{ } \Omega \cdot \text{cm}$, $N_D \sim 1 \times 10^{15} \text{ cm}^{-3}$) was used as the top sliding electrode. The electrodes were cleaned in an ultrasonic tank with acetone, IPA and DI water for 8 minutes sequentially, followed by dipping in 1:10 diluted HF (49%) for 1 minute to etch away native oxide layer. A 10nm Al/100nm Au contact pad was then deposited on the non-polished (back) side for p-type electrode and a 10-nm Ti/100-nm Au contact pad for n-type electrode using an e-beam evaporator. Followed with a rapid thermal process (RTP) in nitrogen gas (N_2) at 380 °C for 30 s.

6.2.2 Setups for the measurement

The surface chemical potential difference between the two electrodes was measured beforehand based on the variable capacitance method described in Section 5.4.

The two electrodes were connected through an adjustable load resistor R to a low noise current preamplifier (SRS570) with the positive input probe connecting to the p-type electrode while the negative to the load and then to the n-type electrode. The voltage across the R was monitored by connecting a low noise voltage preamplifier (SRS560) in parallel to R , as shown in Figure 6-1. The short circuit current I_{SC} was measured with $R = 0 \text{ } \Omega$ and the open-circuit voltage V_{OC} was measured with $R = \infty$.

Figure 6-1 A 3D schematics for the experiment setup and the external circuit of sliding a $1 \times 1 \text{ cm}^2$ n-type silicon electrode on top of a p-type silicon electrode with 100 g weight on top (not to the scales). [187]

For linear sliding motion, a $1 \times 1 \text{ cm}^2$ as-fabricated n-type Si electrode was slid on a p-type Si substrate under the control of a linear motor (LinMot E1100-GP), the translation stage of the linear motor moved back and forth with controlled speeds and accelerations. The dimension of the substrate was sufficiently large so that the top electrode was always slid within it. For experiments where 1 N contact force was exerted, a 100g weight was loaded on top of the moving electrode.

For continuously sliding motions, a 4-inch p-type Si wafer was fixed on the top of a rotation stage that span at a constant angular speed of 10 rpm. A $1 \times 1 \text{ cm}^2$ n-type Si electrode was then slid on the p-type electrode, maintained 30 mm away from the centre.

6.3 The working principles

Figure 6-2 presents the electron transport while an n-type Si electrode sliding on top of a p-type Si electrode. The surfaces of the semiconductor electrodes are assumed to be ideal so that the impact of surface states on the energy band diagram and electron transfer is not considered. Figure 6-2(a) shows when the electrodes are separated and disconnected, where E_0 is the vacuum level, E_c the bottom of the conduction band, E_v

the top of the valence band, E_i the intrinsic and E_F is the Fermi level where E_{F1} in the p-type lies lower than E_{F2} in the n-type, $q\phi$ is the work function. When a p-type semiconductor is in contact with an n-type semiconductor, due to the difference in chemical potential, electrons diffuse from the n-type to the p-type side, leaving a positively charged space charge region near the surface of the n-type electrode and a negatively charged region for the p-type. At thermal equilibrium, shown in Figure 6-2(b), the drift current originated from the electric field over the space charge regions gradually balances out the diffusion current, and the space charge regions, or a p-n junction, are formed. The built-in electric field points from the positive space charge region in the n-type to the negative space charge region in the p-type side, denoted with the red arrows in Figure 6-2 (b&c). While sliding one electrode on the other, electrons and holes can be excited at the interface due to the friction energy, and the built-in electric field will drive the charge carriers to flow out the junction, resulting in a DC current in the external circuit.

The working principle of the triboelectric cell is essentially different from any electric generators introduced in Section 1.1. The mechanism of solar cells can be used for reference in understanding this triboelectric cell. When light is incident on the p-n junction, electron-hole pairs can be excited by photon energy, and the built-in electric field drives the electrons and holes to flow, resulting in a current constantly flows from the p-type through external load resistance back to the n-type electrode. In this triboelectric cell, instead of photon energy, frictional energy is input, exciting electrons and holes at the contacted surfaces of the dynamic p-n junction. The white arrows in Figure 6-2(b&c) refer to the effective electric dipole formed by the space charges in the p-n junction, more discussions in Section 6.4.4.

Figure 6-2 The schematics and energy band diagrams of sliding an n-type semiconductor on top of a p-type semiconductor. (a) Two electrodes are separated and disconnected; (b) the two electrodes are contacted but not moving; (c) the top electrode is sliding laterally. Where E_c refers to the bottom of the conduction band, E_v the top of the valence band, E_i the intrinsic and E_F is the Fermi level with E_{F1} in the p-type lies lower than E_{F2} in the n-type, $q\phi$ is the work function.

6.4 Results and discussions

6.4.1 Direct current output

Figure 6-3(a) shows an arbitrary cycle of sliding a $1 \times 1 \text{ cm}^2$ n-type Si electrode on a p-type Si electrode back and forth under a normal force of 1 N. Figure 6-3(b) shows the transient current during the four acceleration/ deceleration stages as a function of instantaneous speed. Stages 1 and 3 refer to the motion that the top electrode was accelerated from resting to sliding at 50 mm/s, and Stages 2 and 4 correspond to the period the top electrode arrived at the full stop from constantly sliding, as highlighted in Figure 6-3(a). It is clearly observed that the current was generated instantaneously with the sliding motion, and it always flowed out from the p-type electrode to the external circuit and back into the n-type electrode regardless of the moving direction. A continuous DC current of magnitude around 50 nA was generated when it slid at a constant speed of 50 mm/s. The fluctuation of current during the sliding should be

associated with the microscopic friction instability, which is raised from the friction force variation among discrete contact regimes, such that the relative motion from the microscopic view follows the stick-slip behaviour as introduced in Section 2.1 [37], [188].

Figure 6-3 An arbitrary cycle of transient current generated by sliding a $1 \times 1 \text{ cm}^2$ n-type Si electrode on p-type Si electrode forward and backward under a contact force of 1 N at a constant speed of 50 mm/s. (a) The sliding velocity of the top sliding (the upper panel), and I_{SC} as a function of time (the lower panel) vs time; (b) The transient current during four acceleration and deceleration stages vs instantaneous velocity. The positive probe of current meter connected to the p-type electrode and negative probe to the moving n-type.

Figure 6-4 show the average I_{SC} and V_{OC} for sliding back and forth the n-type electrode on the p-type Si electrode under 1 N over 20 minutes. A 2-second pause was implemented after each sliding to avoid the influence from heat accumulation, and steady output was observed over time. By continuously sliding an n-type Si electrode on a rotating p-type Si electrode, DC current was also generated (see Figure 6-5). The top n-type Si electrode was maintained 30 mm away from the rotation centre, and the angular speed of the bottom electrode was fixed at 10 rpm. The average I_{SC} was around 50 nA, no obvious decay or argumentation in current were observed.

Figure 6-4 Average (a) I_{sc} and (b) V_{oc} under reciprocate sliding a $1 \times 1 \text{ cm}^2$ n-type Si electrode on a p-type Si electrode at 50 mm/s under 1 N over 20 minutes.

Figure 6-5 I_{sc} of continuous sliding by sliding an n-type Si electrode 30 mm away from the rotation centre of a p-type Si electrode rotating at 10 rpm.

Unlike in TENGs where the electrons move under the electrostatic induction between the electrodes, requiring a potential difference by varying the capacitance, such as changing the overlap sliding area; in triboelectric cells, the size of the contacting area is maintained unchanged during sliding, and the electrons and holes are excited by frictional energy and driven by the built-in electric field in the p-n junction, resulting in a DC current. Also, oppositely doped semiconductors are directly used as electrodes in triboelectric cells instead of insulating materials used in TENGs. The charge polarisation is raised from the space charge in the p-n junction for triboelectric cells rather than the electrostatic charges as in the TENGs. While conventional sliding TENGs generate only

displacement current flow alternately between the two electrodes, triboelectric cells generate a conduction current

6.4.2 Influences of contact force

The normal force applied on the sliding electrode was changed from 0.2 N to 5 N. The force was monitored with the force gauge installed beneath the substrate electrode holder. The I_{SC} generated when sliding a $1 \times 1 \text{ cm}^2$ n-type Si electrode on p-type Si electrode at 50 mm/s under different normal forces are shown in Figure 6-6(b). It is clearly shown that larger I_{SC} was generated when the contact force was increased. For example, the I_{SC} increased from 16.5 nA to 89 nA when the force was increased from 0.2 N to 5 N. This enhancement in the current generated during sliding could be contributed by the enlarged frictional power generated according to $P_f = \mu_s F v$, where μ_s is the sliding friction coefficient, F the normal force and v the sliding velocity [19] as introduced in Section 2.1. Also, larger contact force directly result in more intimate contact at the interface, enhancing the formation of the p-n junction, which can be confirmed with the I-V rectification curves across the electrodes, shown in Figure 6-6(b). Under a normal force of 0.2 N, or an apparent pressure of 2 kPa, the rectification factor, defined as $|I_F(V_{bias}=1 \text{ V})| / |I_R(V_{bias}=-1 \text{ V})|$, was only 4.5. Under a larger force of 5 N, or an apparent pressure of 50 kPa, the rectification factor was improved to around 20, indicating a better formation of the junction. Besides, the current under 1 V forward bias increased when the normal force was larger, suggesting a reduced contact resistance at the interface when the force increased. But as Si surfaces are rigid, further increase contact pressures would not continue show enhancement.

Figure 6-6 Influence of contact force. (a) The magnitudes of I_{sc} measured when sliding a $1 \times 1 \text{ cm}^2$ n-type Si electrode on p-type Si electrode at 50 mm/s, and (b) the I - V rectification curves of n-type Si in contact with p-type Si under normal forces ranging from 0.2 N to 5 N.

6.4.3 Influences of speed and acceleration

Figure 6-7(a) and (b) compare the I_{sc} and V_{oc} generated when sliding a $1 \times 1 \text{ cm}^2$ p-type Si electrode on top of a large n-type Si electrode at different speeds while the normal force was fixed to be 1 N. When the electrode was slid at a constant speed, the average I_{sc} increased linearly with the speed: from 28 nA when the speed was 10 mm/s increased to 460 nA when the speed was as fast as 200 mm/s. The enhancement under faster speed can be understood from the friction power P_f generated at two sliding surfaces, which is directly related to the sliding speed v via $P_f = \mu_s F v$ [19]. At a faster sliding speed v , the friction power dissipated in the region increases, which in turn excites more electrons and holes at the contact surfaces, resulting in a larger current. As for V_{oc} , it was observed to increase with faster speeds but quickly reach to a saturated value of 0.31 V. The measured V_{oc} can be regarded as the voltage over the entire parasitic capacitance including the device and the external circuit, thus under a higher electrons and holes excitation rate, the capacitance is charged quicker, showing an increased V_{oc} . However, V_{oc} comes from the accumulation of electrons and holes

accumulated at the two electrodes, its value is dominated by the built-in potential difference over the junction. Figure 6-8 shows the transient current measured as a function of biased voltage for the chemical potential difference determination using the variable capacitance method introduced in Chapter 5. The chemical potential difference was measured to be 0.35 V. Theoretically, the built-in voltage V_{bi} can be calculated as $V_{bi} = \frac{kT}{q} \ln \left(\frac{N_A N_D}{n_i^2} \right)$, which is around 0.8 V for samples used here. The chemical potential difference measured using the variable capacitance methods had a smaller magnitude than the theoretically calculated V_{bi} , mostly due to the non-ideal surfaces, such that the Fermi levels near the surface shifted towards the intrinsic Fermi level and led to a smaller potential difference. Furthermore, the two terminals from the p-type and n-type electrodes were directly connected to a 1 μ F capacitor, the voltage of the capacitor during charging is shown in Figure 6-8(b). The capacitor was charged to 0.28 V with 4 cycles of sliding back and forth at 50 mm/s and reached a saturation afterwards, which was in consistence with the potential difference measured using the variable capacitance method.

Figure 6-7 I_{sc} and V_{oc} generated by sliding $1 \times 1 \text{ cm}^2$ n-type Si on p-type Si under a normal force of 1 N at different constant sliding speeds from 10 mm/s to 200 mm/s. (a) I_{sc} and V_{oc} vs time under different constant sliding speeds; (b) I_{sc} and V_{oc} vs the transient sliding speed.

Figure 6-8 (a) V_{bi} measured using the variable capacitance method; (b) voltage over a $1 \mu\text{F}$ capacitor being charged.

Besides sliding n-type Si electrode on p-type Si electrode, this V_{OC} saturation characteristic was consistently observed between other semiconductors and even with metal electrodes. Figure 6-9 summarizes the V_{OC} and I_{sc} generated while sliding at 100 mm/s under the normal force of 1 N for six other pairs of electrodes, together with the V_{bi} measured using the variable capacitance method, including a) sliding p-type Si on n^+ -type Si, b) sliding p-type GaAs on n^+ -type Si, c) sliding p-type Si on n-type GaAs, d) sliding Al plate on p-type Si, e) sliding Au electrode ($1 \mu\text{m}$ of Au deposited on Al plate using e-beam evaporator) on p-type Si, and f) sliding Al plate on n-type Si electrode. While sliding two doped semiconductors or metals against each other, and the currents were generated and always flowed from the electrode with a lower chemical potential to the other electrode through the external circuit, which follows the direction of the built-in electric field in the junction formed at the contacted surfaces. In addition, the V_{OC} generated when sliding at 100 mm/s for all tested pairs were capped at the value of V_{bi} for all pairs, with a difference in magnitude of not more than 0.05 V. The consistencies in the current generation through sliding and the capped magnitude of V_{OC} further suggest that the electrons and holes are generated under the sliding friction, and the built-in electric field in the junction drives the charge carriers to flow out the junction.

Figure 6-9 The V_{OC} (upper) and I_{SC} (lower) generated by sliding different pairs of semiconductors or metals at 100 mm/s under 1 N normal force. (a) Sliding p-type Si on n^+ -type Si; (b) sliding p-type GaAs on n^+ -type Si; (c) sliding p-type Si on n-type GaAs; (d) sliding Al plate on p-type Si; (e) sliding Au electrode on p-type Si (f) sliding Al plate on n-type Si electrode.

Figure 6-10 shows the current and average power generated in the external circuit when slide the top electrode at a constant speed of 50 mm/s with load resistance R was added. The power delivered to R calculated from I^2R . When the load resistance was around 1 $M\Omega$, the power delivered to the load reached a maximum value of 1.2 nW. To estimate the friction power, μ_s was taken as 0.2 [189], [190]. Thus, the friction power was

estimated to be $P_f = \mu_s F v \sim 10 \text{ mW}$, leading to the efficiency of the power conversion only around $1.2 \text{ nW}/10 \text{ mW} \sim 10^{-7}$.

Figure 6-10 The current and average generated electric power as a function of load resistance connected in the external circuit for sliding $1 \times 1 \text{ cm}^2$ n-type Si on p-type Si at a constant speed of 50 mm/s under a normal force of 1 N.

Besides sliding under constant speeds, the top electrode was also slid with accelerations from 0.05 m/s^2 to 1 m/s^2 . The measured I_{SC} and V_{OC} are shown in Figure 6-11. While I_{SC} increased at a higher instantaneous speed, V_{OC} increased along the time shortly before reaching to the saturated voltage value of 0.35 V, consistent with the V_{bi} . In addition, Figure 6-11(b) shows the I_{SC} at each transient speed under different accelerations, where for the same instantaneous speeds, the higher accelerations, the larger transient current was obtained. For instance, for the instantaneous speed being 100 mm/s, I_{SC} was $0.23 \mu\text{A}$ when acceleration was 0 (the constant speed of 100 mm/s in Figure 6-7), while with an acceleration of 1 m/s^2 , I_{SC} increased to $0.58 \mu\text{A}$, suggesting an enhancement for electrons and holes excitation under the acceleration motion. Indeed, under an acceleration motion, there is an additional term in the friction power ΔP_f generated. From $t = t_0$ to $t = t_0 + \delta t$, ΔP_f can be expressed as $\Delta P_f = P_f|_{t_0 + \delta t} - P_f|_{t_0} = \mu_s F v|_{t_0 + \delta t} - \mu_s F v|_{t_0} = \mu_s F a \delta t$. For a constant speed movement, $a = 0$, $\Delta P_f = 0$. While for

an accelerated movement, the additional power ΔP_f is proportional to the acceleration. As a result, the additional power dissipated to the interface and caused more electrons and holes generation. Moreover, it is self-evident that sliding friction can lead to temperature increase at the surface. Hence, under a constant speed motion or motions with small accelerations, a temperature profile may be formed, through which heat could transport into the bulk of the electrodes, resulting in weaker electron-hole generation at the surfaces.

Figure 6-11 I_{SC} and V_{OC} generated by sliding $1 \times 1 \text{ cm}^2$ n-type Si on p-type Si under a normal force of 1 N at different accelerations from 0.05 m/s^2 to 1 m/s^2 . (a) I_{SC} and V_{OC} vs time under different accelerations; (b) I_{SC} and vs the transient speed under different accelerations.

The I-V rectification curves before and after sliding at 100 mm/s are shown in Figure 6-12(a), where 0 s refers to the moment immediately after the top electrode came to a full stop, while 1 s to 4 s stand for the measurements acquired every 1 second subsequently. The I-V curves indicate the depletion region formation at the contacted surfaces. The current under 1 V forward bias was $35 \mu A$ before sliding, and that was observed to be boosted up to $75 \mu A$ when immediately after the sliding motion, which was more than doubled than before sliding. However, this biased current gradually reduced and recovered to the magnitude measured before sliding during the next 3 to 4 seconds. Furthermore, Figure 6-12(b) shows the I-V rectification curves measured

immediately when the top electrode came to a full stop after sliding at different constant speeds. A general trend that the higher sliding speed the larger biased current measured could be obtained. This enhancement in biased current could be related to the increased friction excited electrons and holes trapping. Due to the non-ideal contact surfaces, some of the excited electrons and holes may get trapped at the intermediate states and form an accumulated region of electrons or holes near the surfaces of the n-side and p-side, showing a temporary enhancement for the depletion region formation. As the trapped electrons or holes could escape and be swept out the junction so that the contacted semiconductors could restore thermal equilibrium quickly, the measured rectification curves gradually recovered, approximately 4 seconds after the electrode stopped sliding.

Figure 6-12 Rectification characteristics for p-n electrodes contacted before and after sliding n-type Si on p-type Si under a force of 1 N. (a) I-V curves before and 0-4 seconds after sliding at 100 mm/s; (b) I-V curves immediately after sliding at different speeds.

6.4.4 Influences of the electrode geometry

The top electrodes with different dimensions, i.e., $1 \times 1 \text{ cm}^2$, $0.5 \times 2 \text{ cm}^2$ and $2 \times 0.5 \text{ cm}^2$ were used. With maintaining the same contact area of 1 cm^2 , normal force of 1 N and sliding speed of 50 mm/s, the average I_{SC} and V_{OC} are shown in Figure 6-13 solid lines. In general, V_{OC} was not sensitive to the dimensions, comparable with the built-in voltage which is determined by the two electrode materials. However, I_{SC} shows a

sensitive dependence on the dimensions, such that I_{SC} increased linearly with the length of the side that is perpendicular to the moving direction (w in Figure 6-1). A similar finding was observed from sliding another set of top electrode dimensions, i.e., $1 \times 2 \text{ cm}^2$, $1.4 \times 1.4 \text{ cm}^2$ and $2 \times 1 \text{ cm}^2$, under the same normal force of 1 N, suggesting that the length of the sliding side dominates I_{SC} . Interestingly, I_{SC} was slightly reduced for the electrodes with an overall area of 2 cm^2 comparing to the 1 cm^2 ones, indicating that a higher pressure could yield a higher I_{SC} , rather than the apparent contact area.

Figure 6-13 I_{SC} and V_{OC} generated by sliding top n-type Si electrode on p-type Si electrode against different lengths of the sliding side while maintained the same apparent contact area at 50 mm/s under 1 N normal force.

At the contact region of the two electrodes, p-n junction is formed. Concurrently, the space charge regions can be regarded as effective electric dipoles whose dipole moments pointing from the negative to the positive space charge. At thermal equilibrium, the dipole moments are perpendicular to the contacted surfaces, denoted with white arrows in Figure 6-2(b). When the top electrode is moved forward, the space charge region in the bottom electrode follows, but with a lagged mismatch of $d \sim v\tau$, where v is the moving speed and τ is the dielectric relaxation time. With assuming the uniform

distribution of the dipoles in the space charge region, a net dipole moment change is formed, and the potential energy in the dipole is increased. The mismatch is then restored and new dipole will be formed (Figure 6-2(c)). Part of the released energy from the newly formed dipole would excite electrons and holes in the newly contacted region with an area of $wd \sim wv\tau$, proportional to w . Then excited electrons and holes will be driven by the built-in electric field and flow out to the external circuit, generating a DC current. As a result, the new overlapping/releasing regions are more directly contributed to the current generation, that is, I_{SC} increases linearly proportional to w , instead of the apparent contact area of the top electrode.

Two 4-inch Si wafers, including one with lightly boron doped p-type and the other with heavily phosphorus doped n-type, were spun along their common central axis with a contact force of 5 N as shown in Figure 6-14(a). I_{SC} of 0.35 μA (Figure 6-14(b)) and V_{OC} of 0.41 V (Figure 6-14(c)) were generated when spinning the top wafer clockwise and counter-clockwise at 30 rpm. This current and voltage generations under fully-overlapped area support the mechanism of frictional power coupling with built-in electric field. Also, this does not necessarily void the proposed picture that the excitation energy origins from potential energy change of the effective dipole moments. Due to the lack of atomic smooth surfaces, the contact was non-ideal. Thus, the p-n junctions formed at the interface were uneven and can be regarded as multiple p-n junction regions connected in parallel. When the top surface was spinning, the individual p-n junction regions were sliding dynamically, and hence generated current even though the apparent contact region were fully overlapped. Also, in the case the two wafers were not perfectly parallel to each other, spinning along one same axis result in unequal pressure, the effective newly swept region as discussed previously became non-fixed, which may explain the output variation.

Figure 6-14 Rotating two 4-inch Si wafers along their common axis with contact region completely overlapped. (a) Schematics of experimental setups; (b) I_{SC} and (c) V_{OC} generated while rotating at 30 rpm.

To compare the influence of the contact surface smoothness on I_{SC} , unpolished surfaces of the Si wafers were used as the sliding surfaces for the top and bottom electrodes alternatively. The top sliding electrode was kept as n-type Si with an area of $1 \times 1 \text{ cm}^2$, and the bottom substrate electrode was always p-type Si. The I-V rectification curves and the I_{SC} against time for each combination are shown in Figure 6-15. When an unpolished surface was only used for either the top or bottom electrode and the other electrode was of a polished surface, a well rectified I-V curve was measured. However, when the unpolished surfaces were used for both electrodes, the rectification was weakened while the currents under both forward and reverse bias were increased. This could be because of that although rough surfaces assisted in asperity contacts so that the contact resistance was reduced. But if both contact surfaces were roughened, the

influence of surface defects became more prominent, led to more severe Fermi level pinning, so that the rectification was weakened.

When a polished top electrode was slid on the unpolished substrate at 100 mm/s under a normal force of 1 N, I_{SC} of up to 250 nA was generated, slightly larger than that generated by sliding the polished top electrode on the polished substrate at the same speed, i.e., around 200 nA, as shown in Figure 6-7(b). The enhancement could be due to the improved asperity contacts caused by the roughness, such that better junctions were formed at the contacts. Surprisingly, when the top electrode was changed to the unpolished surface and the substrate to be with polished surface, I_{SC} reduced significantly to a value of 50 nA, despite the well rectified I-V curve at still. Theoretically, the friction pairs of one roughened surface and one polished surface should have comparable friction coefficients, so that the frictional power induced current generation should be similar. However, it was observed that with roughened top electrode sliding, severe scratches were quickly built up on the surface of the bottom electrode. These surface scratches introduced defects into the interface; also, they were the signs of material wearing due to sliding, such that the particles from the bottom electrode detach from the original surface and adhere to the top electrode, and same for the top electrode. Consequently, the rate to form new junctions along sliding decreased, resulting in smaller current output. Similarly, when both rough electrodes were used, the theoretical value of the friction coefficient increased, but the output current was not significantly improved, with a peak value of more than 200 nA, and the stability was inadequate. As the p-n junctions formed at the rough surfaces were non-uniform, when the top electrode slid forward, the overall rate for newly formed junctions in the front and the ones disappear at the rear was random, leading to fluctuated current generation.

Figure 6-15 Influences of the surface roughness. (a) The I-V rectification curves and (b) I_{sc} for sliding n-type Si on p-type Si at 100 mm/s under a normal force of 1 N with different combinations of unpolished and polished surfaces.

6.4.5 Influences of environmental effects

It is known that electrostatic breakdown between two charged surfaces can lead to current generation. Some direct-current triboelectric nanogenerators based on electrification effect and electrostatic breakdown were reported. For example, Liu et al. [146] reported a TENG that consists of a PTFE triboelectric layer, a Cu frictional electrode and a charge collecting electrode that was connected to the frictional electrode through the external circuit. The charge collecting electrode was fixed at a tiny distance from the PTFE surface, such that when the frictional electrode was slid on the PTFE surface, electrons first transfer to PTFE via triboelectrification and induce positive charges in the collecting electrode nearby, causing electrostatic breakdown when the electric field built was high. The electrons discharged during electrostatic breakdown then flow from the charge collecting electrode to the frictional electrode via external circuit, resulting in constant DC current generation.

As in a triboelectric cell, the contact is non-ideal, the air gaps at the contact surfaces as unavoidable. When two oppositely doped semiconductor electrodes are in contact, their

Fermi levels align, and the built-in electric field is formed across the p-n junction. With this built-in electric field over the tiny gaps, it is reasonable to consider the possibility that the electrons are due to discharge under electrostatic breakdown. However, this mechanism is not applicable to our triboelectric cell. Put aside the limited magnitude of the built-in potential, the experimental results did not support the occurrence of electrostatic discharge of the air molecules trapped at the contacted surfaces. If electrostatic discharge would happen, a DC current could be detected once the electrodes are contacted, and it would not be promoted by the sliding. In fact, as shown in Figure 6-3(b), the instantaneous current was generated only when there was relative sliding. To further investigate the influence of the air pressure, the electrodes were installed in a vacuum chamber and slid under different air pressure. Based on Paschen's law, in which the breakdown voltage V_B is described by the equation [191]:

$$V_B = \frac{Bpd}{\ln(Apd) - \ln\left[\ln\left(1 + \frac{1}{\gamma_{se}}\right)\right]} \quad (6.1)$$

where p is air pressure, d is the gap between electrodes, A and B are experimentally decided constants related to the property of given gases, γ_{se} is the secondary-electron-emission coefficient for the electrodes. By reducing the value of pd , the V_B varies according to Paschen's curve. If the current would originate from air breakdown, the current should be sensitive to the air pressures in the chamber due to the variation of the breakdown voltage. However, as shown in Figure 6-16, with gradually pumping down the chamber, I_{SC} measured remained constant, showing no significant enhancement or decay. After being pumped to a high vacuum level of pressure of 10^{-5} Pa, the chamber was refilled with N_2 gas up to the atmospheric pressure and tested again. As shown in Figure 6-17, the measured I_{SC} was comparable to all the other conditions, suggesting the

current generation is independent of gas/ air pressure, suggesting that the generated DC current was not due to an electrostatic breakdown of air or pure nitrogen molecules.

Figure 6-16 I_{sc} for sliding under different air pressures in the chamber.

Figure 6-17 I_{sc} measured in the vacuum (10^{-5} Pa) and nitrogen/air atmosphere (10^5 Pa).

Theoretically, the strength of the built-in electric field in the contacted p-n junction is not sufficient for air breakdown either. First, the electrodes used in the experiments were doped semiconductors, the maximum electric field E_{max} at the ideal contact p-n junction can be calculated via $E_{max} = -(2q/\epsilon N_A V_{bi})^{\frac{1}{2}}$, where q is the unit charge, ϵ is the permittivity of Si, N_A the accept doping concentration. For the two semiconductor

electrodes used here, $E_{max} \sim 3 \times 10^6$ V/m. Note that, for tiny gaps below 5 μm , the electric field for air breakdown is 10^8 V/m [192]–[194], which is two orders higher than E_{max} . Considering the abundant surface states as well as the non-ideal p-n junction, the actual electric field in the junction should be even lower, insufficient for air breakdown to happen.

Meanwhile, the possibility that the current is generated due to the ionisation of moisture in the air can be eliminated too. In the low air pressure, e.g. 10^{-5} Pa, the desorption rate of water molecules is greatly increased than in the atmosphere, dramatically reducing the amount of water molecules absorbed on the surface, but the current was generated steadily, showing that moisture is not a necessary factor for the current generation.

Temperature is another factor that could affect the current output. Figure 6-18 shows the average I_{SC} and V_{OC} generated when the temperature was increased from the room temperature up to 120 °C, the chamber had been pumped down to an air pressure of 10^{-5} Pa in advance to avoid surface oxidation. While the temperature gradually increased, the average I_{SC} dropped from 150 nA at the room temperature to only 50 nA at 120 °C, and the average V_{OC} also decreased from 0.33 V to 0.13 V. The reduction was contributed to decreased V_{bi} . With increasing temperature, the V_{bi} becomes smaller as the Fermi levels in both semiconductor materials shift towards the centre of the bandgap. Theoretically, V_{bi} would drop from 0.84 V at room temperature to 0.69 V at 120 °C, reduced by $(0.84-0.69)/0.84 \sim 18\%$ of the magnitude of V_{bi} at room temperature. Taking the non-ideal contact into consideration, the reduction in V_{bi} could be more severe. The I-V rectification curves under several temperatures are shown in Figure 6-19. With increasing the temperature, the currents under both forward and reverse bias also decreased because of weakened p-n junction. Furthermore, as shown in Figure 6-20, the maximum electric power dissipated on the load resistance decreased from around 18

nW at room temperature to only 2 nW at 80 °C. The decline in generated electric power output is consistent with the weakened p-n junction.

Figure 6-18 (a) I_{sc} and (b) V_{oc} measured in vacuum (10^{-5} Pa) as a function of temperature under a normal force of 1 N and sliding at a speed of 100 mm/s.

Figure 6-19 The I-V rectification curves under different temperatures.

Figure 6-20 The generated electric power delivered to external load resistance at 25 °C, 40 °C, 60 °C and 80 °C by sliding 1 cm² n-type Si electrode on p-type Si electrode at 100 mm/s under a normal force of 1 N and an air pressure of 10⁻⁵ Pa.

6.4.6 Sliding on wet surfaces

For any TENG devices, the presentence of water layer would dramatically suppress the current generation, caused by the surface charge discharging due to the increased surface conductivity[99]. Different from TENGs, as shown in Figure 6-21, the current generated from sliding an Al plate on a p-type Si electrode was found to be greatly boosted from around 40 nA for dry surface up to more than 100 nA after introducing DI water to the sliding surfaces. In contrast, when lubrication oil (consists of distillates (petroleum)) was added to the interface, the current reduced significantly to a magnitude smaller than 5 nA. The current generation enhancement by adding DI water could be attributed to the conductivity of the thin water layer, so that the tiny air gaps at the contact interface can be partially filled with a thin layer of water molecules, which increases the effective contact area, resulting in a smaller average contact resistance; whereas adding oil may adverse the formation of the junctions due to the presence of other impurities. It is worth noting that when DI water was added in, a non-zero current was observed even when

the two electrodes are still. This may be related to the discharging from the double-layer capacitance formed at the interface of water and semiconductor surfaces.

Figure 6-21 I_{sc} comparison of sliding a 1 cm^2 n-type Si electrode on p-type Si electrode at 50 mm/s under a normal force of 1 N on the dry surface, surface with water layer and surface with an oil layer.

6.5 Conclusions

In this chapter, direct current generators by sliding a doped semiconductor or a metal electrode on another doped semiconductor electrode are introduced and studied. As long as the two materials possess distinct work functions, a DC current could be generated by relative sliding, and the generated current flow from the electrode with higher work function through the external circuit back to the one with lower working function. The mechanism was discussed. We propose that the electrons and holes are generated by friction power exerted at the sliding surfaces, and the built-in electric field of the dynamic semiconductor junctions drives carriers to flow out. The direction of the current is essentially determined by the built-in electric field of the p-n or Schottky junction formed at the contacted interfaces. The current increases with sliding speed while the open-circuit voltage is restrained by the built-in potential of the junction. The influences

of the electrode geometries including area, side length and roughness are studied and it was observed that the side length that is perpendicular to the sliding direction is more efficient in increasing current generation rather than the overall contact area. The current was found to be independent of air pressure and the moisture adsorbed on the surface, but increasing temperature resulted in reduction of both I_{SC} and V_{OC} measured, mainly due to the narrowing effect of built-in voltage. The findings suggest that electrons and holes are generated possibly due to friction power that is used to engage the change of the dipole moments that are formed by the dynamic space charge regions. The current generation in our generators shares many similarities with a semiconductor solar cell. The major difference lies in the carrier generation by friction power, rather than by light illumination in solar cells. Different from traditional triboelectric generators, the electric power generation in our generators is not deteriorated in high humidity environment. In fact, the current output is found to be enhanced with lubrication of water.

Chapter 7   Conclusions

7.1   Conclusions

In the first part of this thesis, based on the contact electrification between solid-liquid materials and electrostatic induction, a water sensor for metal ion detection was developed. After dipping a PET film in water samples containing different metal ions, it was found that electrostatic charges remained on the film decreased with a higher ion concentration as well as the increased acidity/alkalinity. Thus, by measuring the electrostatic charges remained on a PET film after dipping, a quick prediction of metal ions concentration and pH level could be obtained. Depending on the electronegativity of individual ions as well as the adhesion strength with PET, the detection limit (the minimum concentration of ions can be detected) can cover the concentration ranges recommended by World Health Organization (WHO). We suggest that the selectivity can be enhanced by treating the polymer surface with targeting metal ions. The thesis then moved to the contact electrification between solid-solid and studied TENGs. Apart from existing complicated fabrication techniques to improve the device performance, three surface modification methods including to use pressed metal foams, to create porous surface structure for contact metal via oxidization and reduction processes, and to roughen contact electrode with sandpaper were performed. The compacted porous structure obtained by pressing a 200 μm porous sized Ni foam down to 50 μm thickness improved the short circuit current I_{SC} by 30% compared to using plain Ni foil. Also, after treating Ni foil under oxidation and reduction processes, refined porous structures were achieved, which could double the magnitude of I_{SC} . In addition, I_{SC} was doubled by polishing the contact electrode with sandpaper. These methods were found to be efficient in increasing the current output, providing alternative engineering solutions for

performance improvement with the least requirement for costly fabrication processes. Furthermore, the influences of contact/separation frequency and load resistance on the device performance were investigated. With increasing the operation frequency, I_{sc} increases linearly with frequency, while the open-circuit voltage V_{oc} maintains relatively constant. On the other hand, high frequency and large load impede charge to flow in the circuit because of RC time. With identifying this limitation, two novel types of generator were proposed in the latter parts of this thesis, intending to provide solutions to mitigate drawback.

In the second part of the thesis, a novel type of generator that generates both conduction current and displacement current was first time developed to reduce the limitation from RC time. By intermittently separating and contacting two oppositely doped semiconductor electrodes, the charges within the space charge regions are extracted into the external circuit repeatedly. The theoretical model for the generators was developed, and a comprehensive study with protocol devices was demonstrated. As the electrodes are semiconducting, space charge restoration can be accomplished via both electrostatic induction and electron diffusion when contacting, one-direction dominated current was observed especially when the external load R is larger than $1\text{ M}\Omega$. The charge generated increases for electrodes with larger contact area, and for Si electrode, electron diffusion can be enhanced after surface treatment by dipping in HF. For the contact/separation frequency from 1 Hz to 10 Hz and load resistance from zero to $1\text{ G}\Omega$, the average charge generation rate increases with enlarged RC time in the circuit, suggesting that our generator has great potential to be used under a broad range of operating frequency, and with higher frequency, this one-direction dominated current generation can be achieved with even smaller R .

Last, in the third part of the thesis, another novel electric generator that generates direct current by sliding a doped semiconductor or a metal electrode on another doped semiconductor electrode was introduced for the first time. The mechanism that electrons and holes are generated under friction power and are subsequently swept out the p-n or Schottky junction was proposed. The direction of the current generated is consistent with the built-in electric field of the junction, and the magnitude of I_{SC} increases with the contact force and sliding speed owing to higher friction power, while V_{OC} is capped at the chemical potential difference between two electrodes. The influences of the geometries of the sliding electrode were studied via changing area, side length and surface roughness. We found that longer side length is more efficient in current generation rather than the overall area, suggesting the energy for electrons and holes excitation could originate from the potential energy released from the dipole moment change during sliding. The current is independent of air pressure and the moisture adsorbed on the surface. But the magnitudes of I_{SC} and V_{OC} reduce with higher temperature, owing to the narrowing effect of built-in voltage. This generator has many similarities with a semiconductor solar cell, while the friction power generates carriers rather than light illumination.

The two novel types of generators developed in this thesis are working with mechanisms very differently from existing electric generators: electromagnetic generators, piezoelectric generators, electrostatic generators, and triboelectric nanogenerators if the including electrification mechanism. Clearly, neither magnetic field nor piezoelectric materials are involved in our generators. It would be worth to have a comparison summary among our generators with existing TENGs, where the devices all work with triboelectric behavior between two electrodes. Some key features are summarized in Table 7-1.

Table 7-1 Comparisons among our generators with TENGs

	Triboelectric Cells	Intermittent pumping p-n junctions	TENGs
Mechanism	Frictional power coupling with built-in electric field	Dual space charge region restoration processes	Triboelectrification and electrostatic induction
Charge	Electrons/ holes flow across the contact region	Electrons/holes diffuse and chemical potential difference induced electrons	Immobile electrostatic charges induced electrons
Current generation	DC, consistent with built-in e-field Conduction current	One-direction dominated Both displacement and conduction current	AC, under capacitive coupling Displacement current
Voltage generation	Low, <1 V Limited by built-in potential difference		Very high Limited by dielectric breakdown
Electrodes materials	Semiconductor or metal		At least one insulating material

7.2 Future work

In this thesis, a generator that consists of two oppositely doped semiconductor electrodes was introduced.

Indeed, the generators are still in protocol stage. There are some limitations we need to solve to push it in real application. First, it is known that the contact of two flat surfaces are still limited to asperity contacts, in which air gaps at the interface are unavoidable. As a result, the p-n junctions are formed at very limited points. Hence, approaches to increase the contact efficiency can greatly improve the performance. For example, to fabricate the generator with semiconductor nanowires and other flexible semiconducting or metallic materials.

Second, at the surface of a semiconductor crystal are full of dangling bonds. In experiments, those dangling bonds are relaxed by either forming bonds with the neighboring bonds or atoms. Also, the bandgap of an ideal Si surface is larger than the relaxed ones. When a p-n junction is formed with those relaxed surfaces, the electron transfer at the interface is hindered. Therefore, efficient surface passivation processes could be a research direction to ease this issue.

Third, our two generators can produce conduction currents, showing promising potential in high frequency applications. Thus, one of our future work would be fabricate micro-scale devices using MEMS techniques with structures capable for vibration in broad frequency range. As semiconductor or metal electrodes are directly used in the generators, they can be seamlessly integrated with electric devices.

Last, note that for TENGs, humidity is unfavorable due to the surface charge being discharged through water layers, very few applications have been developed for wet environment. However, when DI water was introduced at the sliding surface in this generator, a significant boost of current was observed. This provides an alternative solution to replace TENGs to work in humid environments and create DC current without rectification. Meanwhile, it was observed that a non-zero current was generated once there is liquid introduced at the interface even without sliding motion. Further investigation is required for an in-depth understanding.

Author's Publications

Journal paper

[1] R. Xu, Q. Zhang, J. Y. Wang, D. Liu, J. Wang, and Z. L. Wang, "Direct current triboelectric cell by sliding an n-type semiconductor on a p-type semiconductor," *Nano Energy*, p. 104185, 2019.

[2] Q. Zhang, R. Xu, and W. Cai, "Pumping electrons from chemical potential difference," *Nano Energy*, vol. 51, pp. 698–703, 2018.

Patent application

Zhang Qing; Wang Zhong Lin; Wang Jie; Xu Ran. *Triboelectric Cells*. 10201906752T Singapore, 22/07/2019.

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