Master's Thesis
석사 학위논문

Selective Growth of ZnO nanowires for Electronic Skin

Yeri Jeong(정 예 리 鄭 禮 理)

Department of Information and Communication Engineering

정보통신융합공학전공

DGIST

2014

Master's Thesis
석사 학위논문

Selective Growth of ZnO nanowires for Electronic Skin

Yeri Jeong(정 예 리 鄭 禮 理)

Department of Information and Communication Engineering

정보통신융합공학전공

DGIST

2014

Selective Growth of ZnO nanowires for Electronic Skin

Advisor : Professor Jae-Eun Jang

Co-advisor : Professor Hongsoo Choi

by

Yeri Jeong
Department of Information and Communication Engineering
DGIST

A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Master of Science in the Department of Information and Communication Engineering. The study was conducted in accordance with Code of Research Ethics[1]

01. 10. 2014

Approved by

Professor Jae-Eun Jang ______(Signature)
(Advisor)

Professor Hongsoo Choi ______(Signature)
(Co-Advisor)

[1] Declaration of Ethical Conduct in Research: I, as a graduate student of DGIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.

Selective Growth of ZnO nanowires for Electronic Skin

Yeri Jeong

Accepted in partial fulfillment of the requirements for the degree of Master of Science

01. 10. 2014

Head of Committee ________________(인)

Prof. Jae-Eun Jang

Committee Member ________________(인)

Prof. Hongsoo Choi

Committee Member ______________(인)

Prof. Ji-Woong Choi

MS/IC
201222013

정 예 리. Yeri Jeong. The Growth of ZnO nanowires for Electronic Skin. Department of Information and Communication Engineering. 2014. 60p. Advisors Prof. Jae-Eun Jang, Prof. Co-Advisors Hongsoo Choi.

ABSTRACT

Touch sensors have studied intensively to mimic the sense of human touch by using resistive, or capacitive sensors and so on for mobile devices and android robot. However, most of touch sensors simply detect pressure or pressure distribution without psychological feelings such as soft, roughness or pain. To produce artificial psychological feeling, we tried to develop touch sensor arrays based on piezoelectric. Touch sensors based on piezoelectric materials have several advantages such as self-powered, high resolution, multi touch, and simple design. Various piezoelectric characteristics of ZnO nanowire have been studied for a novel tactile sensor concept. To make device structure with high performance efficiency, the crystal orientation of seed layer, the kind of metals, the length of wire, the change of pressure, and the cell size effect have been studied in the point of piezoelectric effect. The combination of Au electrode and thin ZnO seed layer formed by sputtering at room temperature shows a good piezoelectric power generation from the grown ZnO nanowire, since ZnO nanowires on the gold (Au) layer makes a Schottky barrier with good crystallinity. The length of ZnO nanowires are proportional to the growth time. With increasing length of wire, the electrical signal was increased from about 80 mV to 150 mV. The current was also increased from 250 nA to 400 nA. Smaller cell structure produces higher piezoelectric power density due to the increase of effective edge area. Because the resolution of human fingers is very small, about $1mm^2$, the small size effect of ZnO wire array cell gives other design merit for touch sensor application. To produce touch feeling using ZnO wire sensor concept, 3x3 array patterns were fabricated, and then, the power signals were measured when giving external pressure by using several material such as sharp tip or blunt tip. The generated signals are different with materials, shapes and degree of pressure. Therefore, we can produce some psychological feelings using the ZnO wire array structure and signal processing. Since the maximum of process temperature growing ZnO is 90°C, the structure design and fabrication process is quite proper to apply to a flexible substrate and tactile sensor concept. This result can be applied to other fields such as self-power generation or piezo-mechanical device.

Keywords: ZnO nanowires, Piezoelectric, nano-generator, touch sensor;

Contents

List of Figures

Ⅰ. INTRODUCTION

1.1 Motivation

People have many opportunities to shake hands in their life. This simple act can allow people to feel many things such as the other person's strength, emotion, and so on. The skin is the body's largest organ. It covers the entire body and detects contact and sends a variety of information to the brain. Especially, the skin on one's fingers is very sensitive and can detect textures, hardness, and so on. Therefore, it is important to interact with others through the sense of touch.

Nowadays, the general trend is touch screens and their core technology is touch sensors. People can touch the screen of a mobile phone with their hand and this allows them to see what they want to see. The mobile phone has gradually satisfied human's sensibility. Also, interest in and development of touch sensors that imitate the human sense of touch has increased. These sensors can be applied to android robots or implanted in the human body to support disabled people.

Many research groups have studied touch sensors similar to the sense of human touch by using resistive, or capacitive sensors and so on [1]-[3]. Because the resolution of human fingers is very small, near 1mm, the touch sensor should be fabricated to a very small and array shape. However, there have been difficulties to make tiny arrays. Also, existing touch sensors simply detect pressure or pressure distribution without psychological feelings such as pain, roughness, texture, and so on. Above all things, the battery consumption of touch sensors is a problem. To solve this problem, a self-powered system is needed. Therefore, the purpose of this research is to develop a self-powered touch sensor using piezoelectric materials that do not require batteries. Also, because piezoelectric materials can translate mechanical energy to electrical energy or the opposite, psychological touch sensation is made by using an electrical signal processing system. ZnO nanowires are optimized piezoelectric materials and can be made to very tiny dimensions. Currently, nano-generators using ZnO nanowires are fabricated [4], and their structure are used for nano-sensors such as UV sensors [5], pH sensors [6], and so on [7]-[9]. However, a touch sensor using nano-generator is not shown not yet. Therefore, in this research, touch sensors will be fabricated to a size of a human body cell by using ZnO nanowires. The individual touch sensors will detect physical pressure, and show what object is.

1.2 Related works

1.2.1 Piezoelectric nano-generator

Various studies using ZnO nanowires were carried out. ZnO is ideal for nano-generators for converting nano-generators for converting nano-scale mechanical energy into electricity owing to its coupled piezoelectric and semiconductive properties. The devices designed based on this coupled characteristic are the family of piezotronics, which is a new and unique group of electronic components that are controlled by external forces/pressure [10]. The structure of the nano-generator is shown in the inset of Figure 1.1.Vertically aligned ZnO nanowire arrays are sandwiched between two layers of metal electrodes. The advantage of using nanowires is that they can be triggered by tiny physical motions and the excitation frequency can be a few Hz to multiple MHz, which is ideal for harvesting random energy in the environment such as from tiny vibrations, body motion, and gentle air flow [11]. Many researchers have developed UV sensors [5], pH sensors [6], gas sensors [7], and so on [8], [9] by using the above mentioned the characteristics and advantages of ZnO and structure of the nano-generator [12] [13].

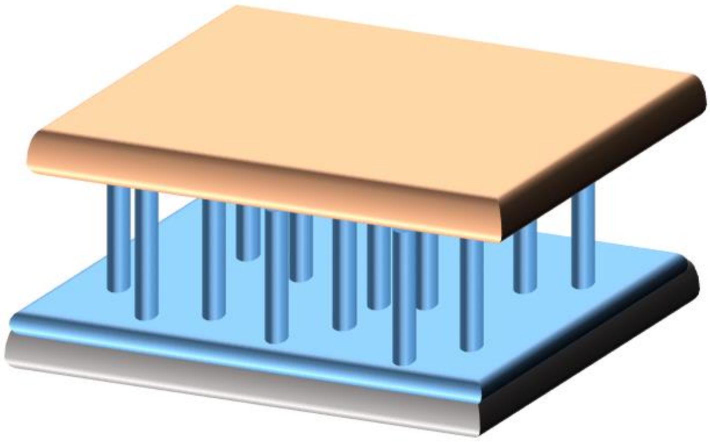


Figure 1.1 A structure of nano-generator using ZnO nanowires

1.2.2 Tactile sensors

1.2.2.1 Capacitive sensors

Capacitive tactile sensors have been widely used in robotics. They can be made very small, which allows the construction of dense sensor arrays. The sensor elements on the array are very sensitive and robust enough to withstand forces during grasping. Capacitive sensing is also popular among the tactile sensors and commercially available touch sensors such as smartphones, tablets, laptops and similar electronic devices are all based on capacitive technology. However, the capacitive sensors only detect anything that is conductive or has dielectric different from that of air. It means capacitive sensors typically do not respond to styluses or gloved hands due to the lack of electrical impulses generated. Therefore, touch sensors based on capacitive mode of transduction are very sensitive, but stray capacity and severe hysteresis are major drawbacks [1] [2].

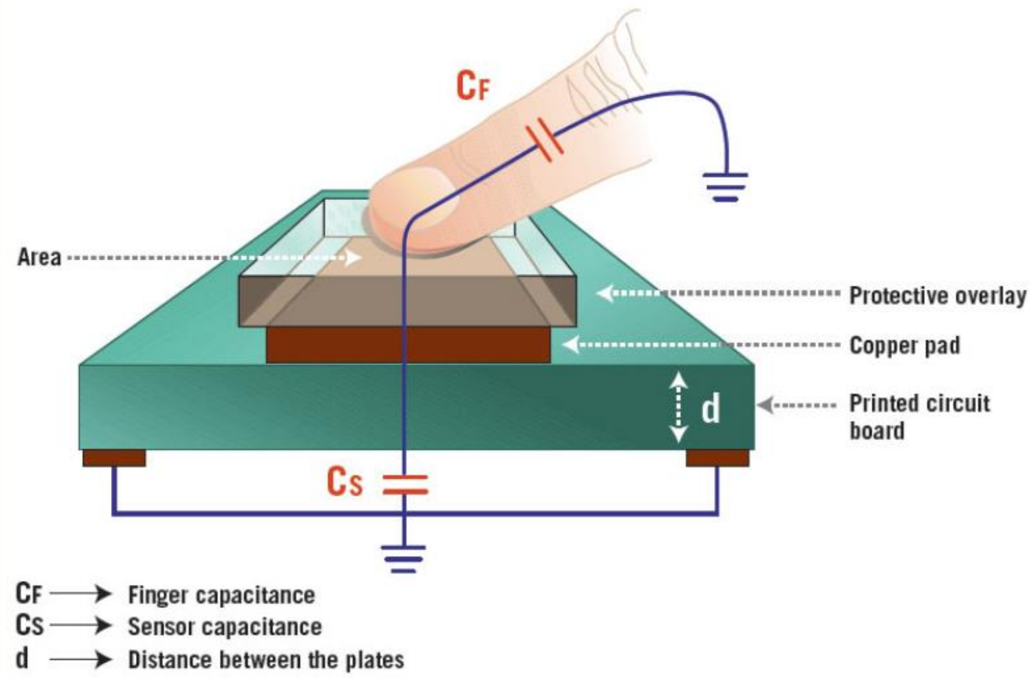


Figure 1.2 The principles of capacitive touch sensing. [30]

1.2.2.2 Resistive sensors

Tactile sensors based on resistive mode of transduction have resistance values depending on the contact location and the applied force. Resistive touch sensors are generally sensitive and economic but consume much power. Their other limitation is that they measure only one contact location. An improved design using parallel analog resistive sensing stripes, which is reported herein, allows the measuring of many contact points. However, the lack of contact force measurement still remains a critical problem. Although resistive sensors have low cost, good sensitivity, low noise, and simple electronics, they also have drawbacks such as nonlinear response, and large hysteresis [1] [2].

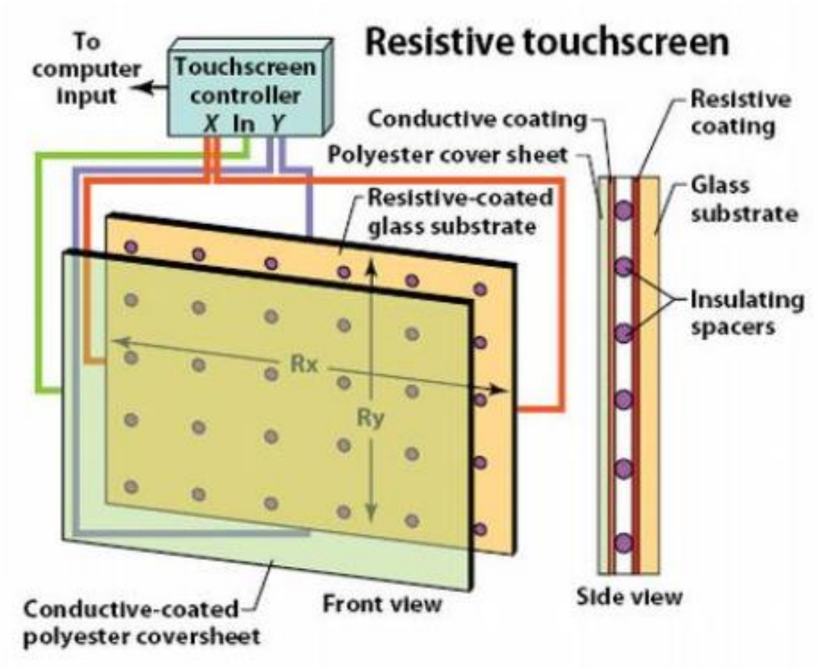


Figure 1.3 The resistive touch screen. [32]

1.2.2.3 Optical sensors

Optical mode sensors use the change in light intensity to measure the pressure at different refractive indices. Optical sensors remains unaffected by electromagnetic interference. They also have high sensitivity for multiple quantities such as temperature and strain, and offer the possibility of measuring at multiple points with one optical fiber. Tactiles using the optical mode of transduction are commercially used. However, because of their high sensitivity, the measurement of one quantity can be influenced by other quantities. Also, they cannot be repaired and have high cost [1] [2].

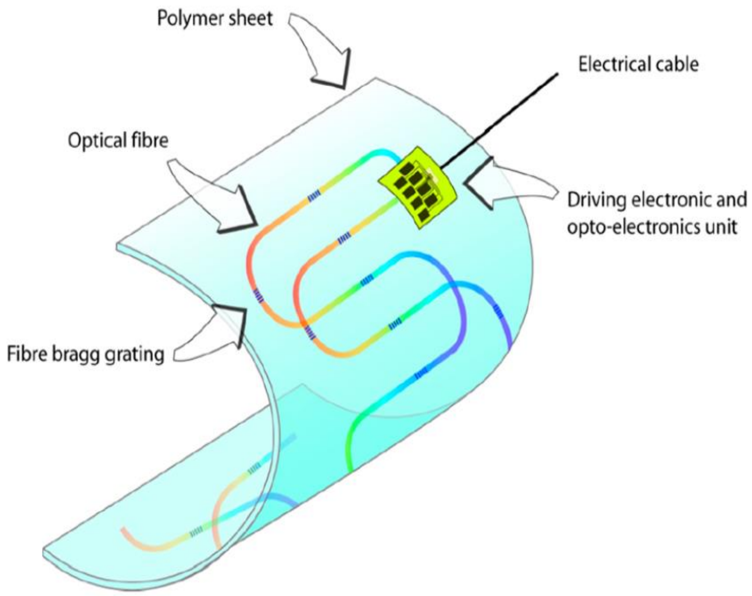


Figure 1.4 Sensing patch with integrated driving electronics and sensing fiber.[33]

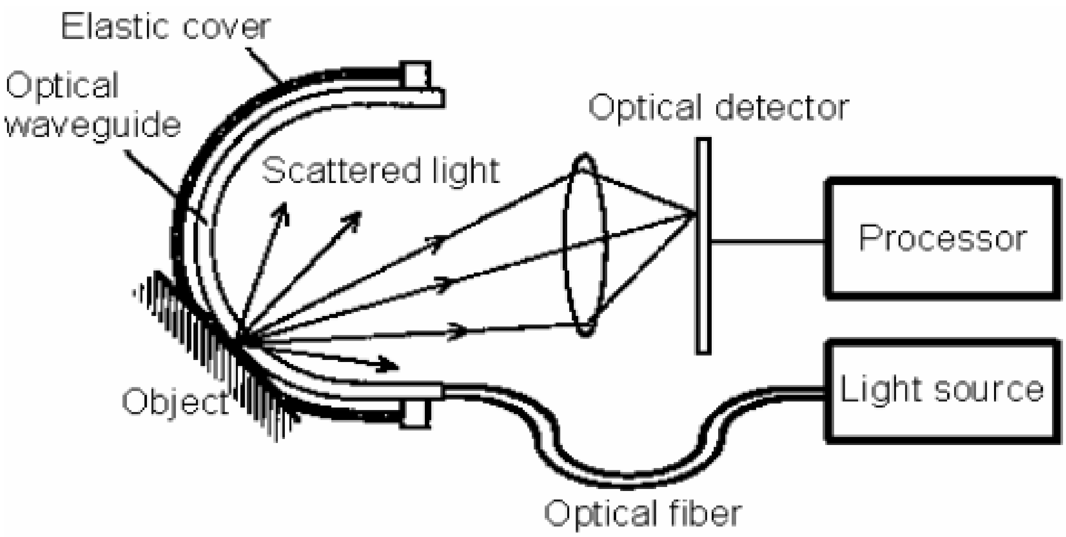


Figure 1.5 The principle of optical tactile sensing.[34]

1.2.2.4 Piezoelectric sensors

Some materials such as quartz, ceramics, and polymers have piezoelectric properties and can be used for dynamic textile sensing. The piezoelectric materials generate charge in proportion to the applied force or pressure. Generally, polymer polyvinylidene fluoride

(PVDF) and ceramic lead zirconium titanate (PZT) are widely used materials. Though quartz and ceramics (e.g., PZT) have better piezoelectric properties, polymers such as PVDF are preferred in touch sensors due to their excellent features like flexibility, workability, and chemical stability. However, the piezoelectric materials are concerned with temperature sensitivity [1] [2].

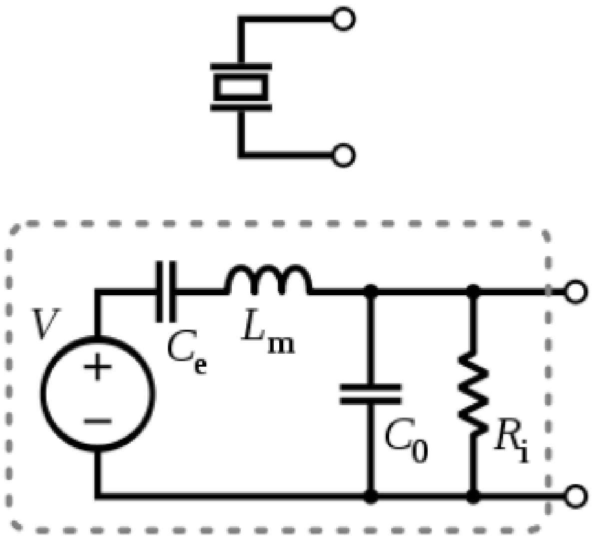


Figure 1.6 Piezoelectric sensor electrical model.[35]

1.2.2.5 Magnetic sensors

Changes in magnetic flux density are the most used principles in magnetic textile sensors. Magnetic textile sensors have many advantages that include high sensitivity, good dynamic rage, no measurable mechanical hysteresis, a linear response, and physical robustness. However, they still fail to be a valuable alternative to the other types of textile sensors. Therefore, their usage is limited [1] [2].

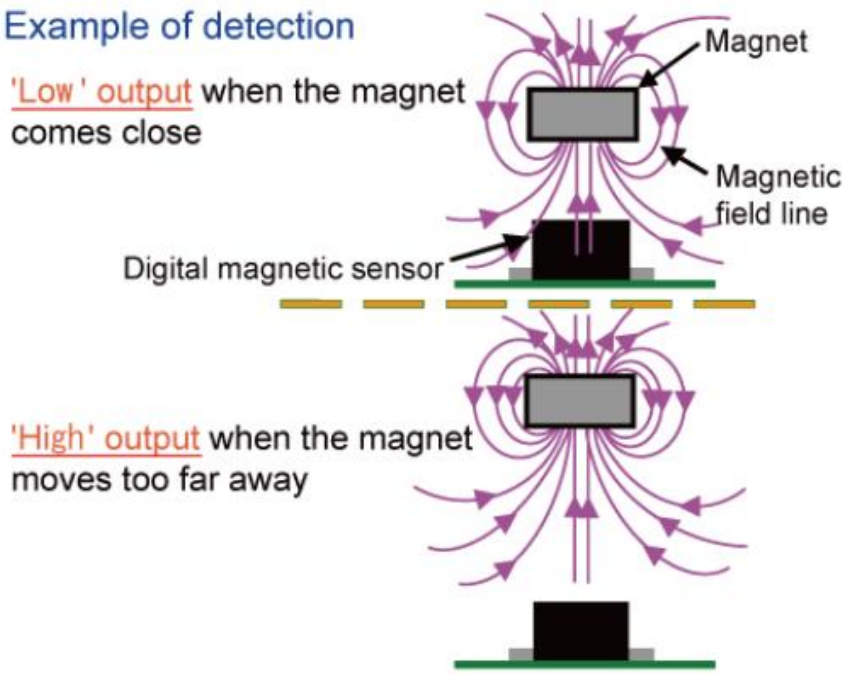


Figure 1.7 The principle of magnetic touch sensing.

1.3 Theoretical background

1.3.1 Piezoelectric

Certain crystals become polarized when they are mechanically stressed. Charges appear on the surfaces of the crystal, as depicted in Figure 1.8(a) and (b). The appearance of surface charges leads to a voltage difference between the two surfaces of the crystal. The same crystals also exhibit mechanical strain or distortion when they experience and electric field, as shown in Figure 1.8(c) and (d). The direction of mechanical deformation depends on the direction of the applied field, and the polarity of the applied voltage. The two effects are complementary and define piezoelectricity.

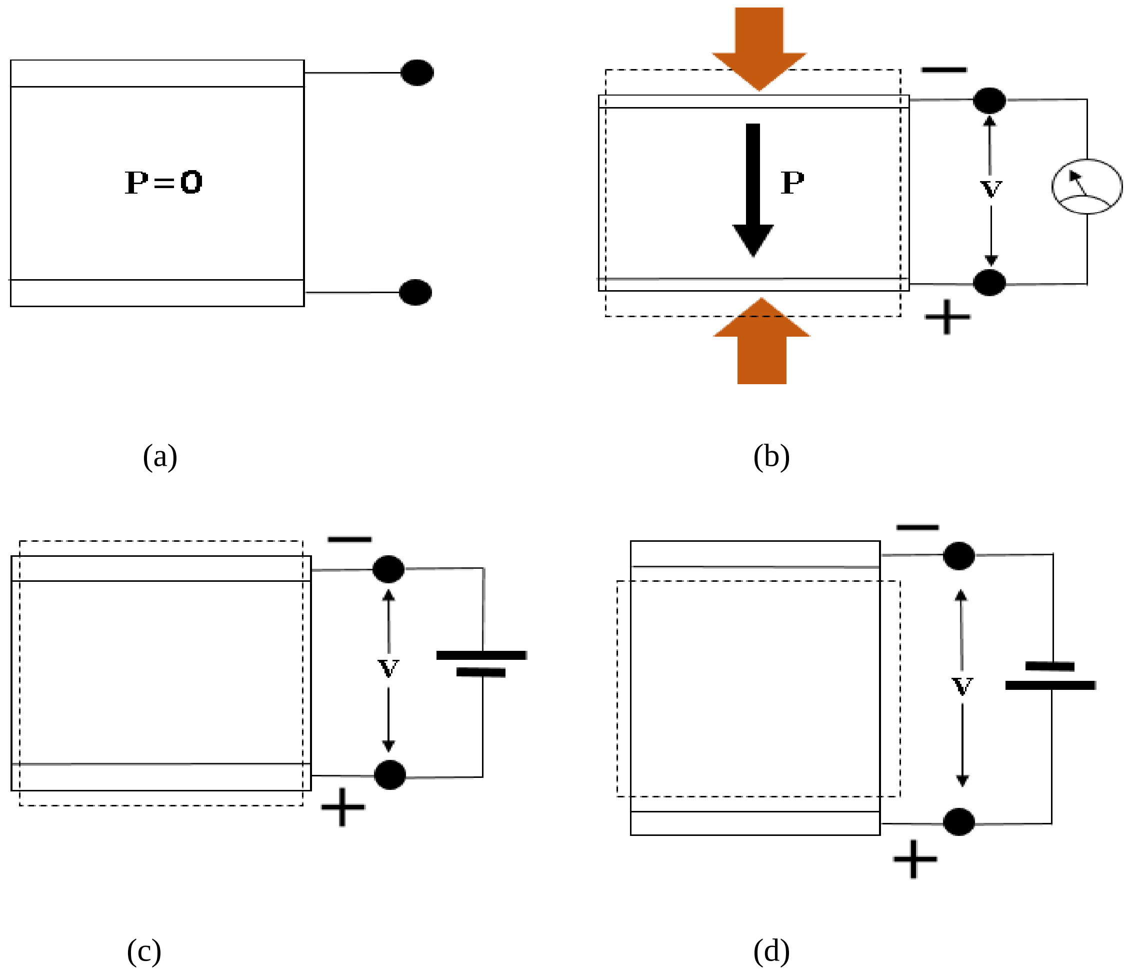


Figure 1.8 The piezoelectric effect. (a) A piezoelectric crystal with no applied stress or field. (b) The crystal is strained by an applied force that induces polarization in the crystal and generates surface charges. (c) An applied field causes the crystal to become strained. In this case the field compresses the crystal. (d) The strain charges direction with the applied field an now the crystal is extended.

Piezoelectric crystals have no center of symmetry. For example, the hexagonal unit cell shown in Figure 1.9(a) exhibits no center of symmetry. When unstressed, as shown in Figure 1.9(b), the center of mass of the negative charges coincides with the center of mass of the positive charges, both at O. However, when the unit cell is stressed, as shown in Figure 1.9(c), the positive charge at A’ and the negative charge at B’ both become displaced inwards to A and B, respectively. The two centers of mass therefore become shifted and there is now a net polarization P. Thus, an applied stress produces a net polarization P in the unit cell, and in this case P appears to be in the same direction as the applied stress, along y. [25]

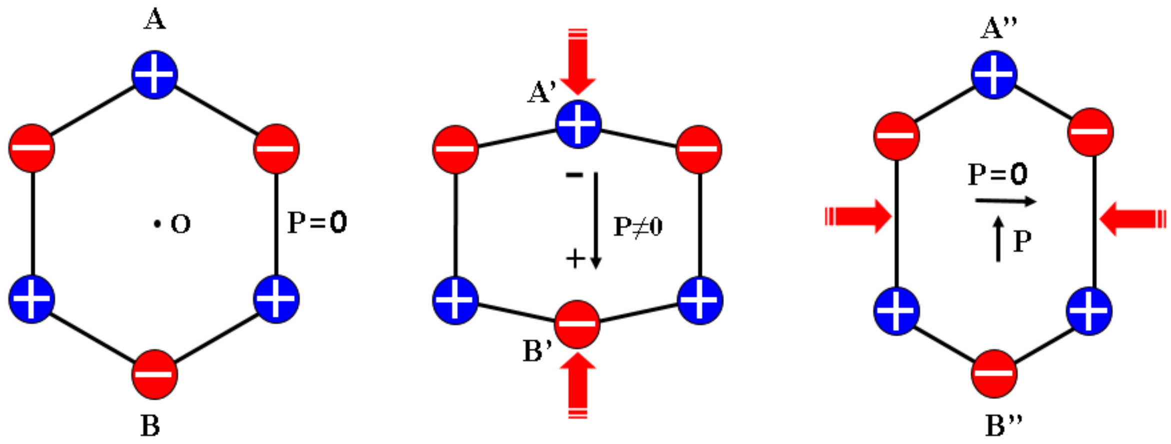


Figure1.9 A hexagonal unit cell has no center of symmetry. (a) In the absence of an applied force, the centers of mass for positive and negative ions coincide. (b) Under an applied force in the y direction, the centers of mass for positive and negative ions are shifted, which results in a net dipole moment, P, along y. (c) When the force is along a different direction, along x, there may not be a resulting net dipole moment in that direction through there may be a net P along a different direction (y).

1.3.2 ZnO

ZnO is a promising semiconductor material with a wide direct band gap of 3.34 eV and large exiton binding energy of 60 meV [14] [15]. It has several properties such as high transmittance, conductivity, and so on. It is also a unique material that exhibits piezoelectric [16], [17] and pyroelectric multiple properties [18]. Therefore, ZnO has been studied in the domain of UV luminescence, solar cells, gas sensors, bio/chemistry sensors, and so on [5]-[9].

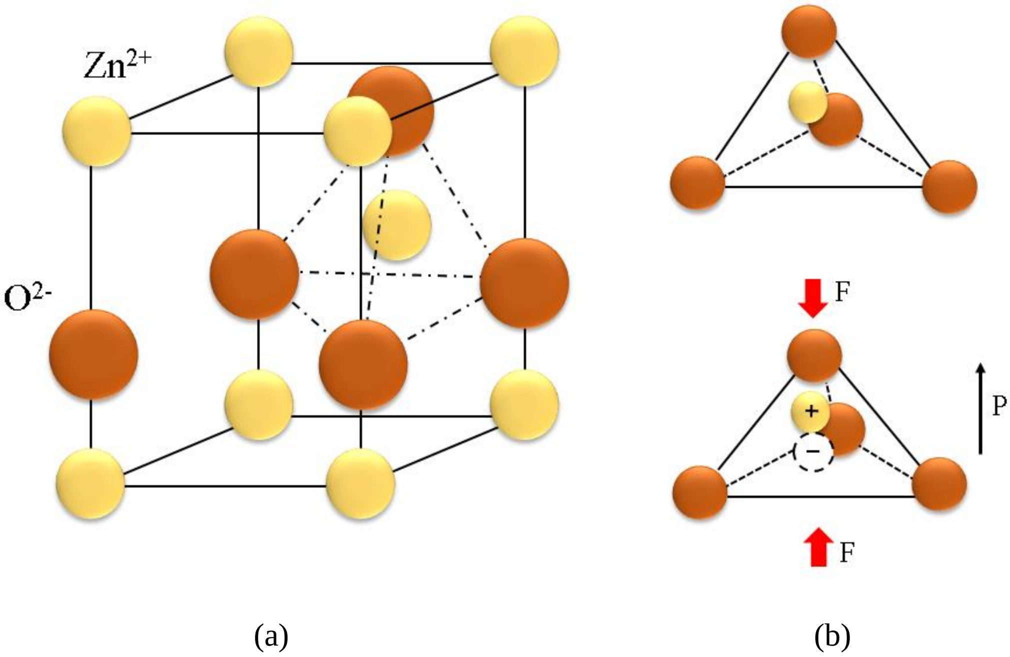


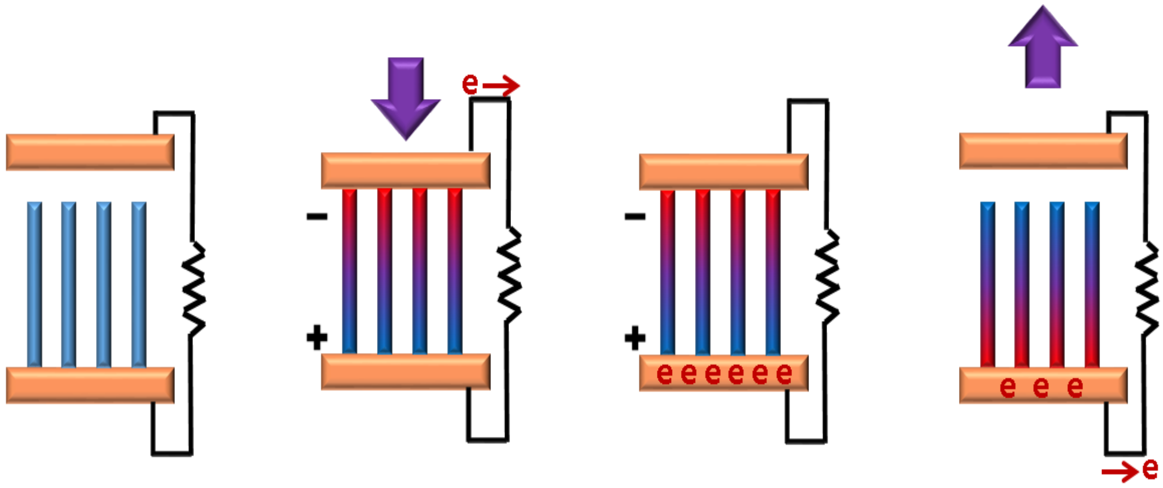
Figure 1.10 A Wurtzite structure model of ZnO, which has non-central symmetry and piezoelectric effect. (a) Structural model of wurtzite ZnO. (b) Schematics showing piezoelectric effect in tetrahedrally coordinated cation-anion unit.

Under conventional conditions, ZnO has the wurtzite structure, which has a hexagonal unit cell with space group of C6mc and lattice parameters a=0.3296, and c=0.52065 nm. The oxygen anions and Zn cations form a tetrahedral unit. The entire structure lacks a central symmetry. As shown in Figure 1.10 (a), the structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternatively along the c-axis [14] [19].

Piezoelectricity is an intrinsic property of ZnO, and it due to the atomic scale polarization. As shown in 1.10 (b), one considers an atom with a positive charge that is surrounded tetrahedrally by anions. The center of gravity of the negative charges is at the center of the tetrahedron. By exerting a pressure on the crystal along the cornering direction of the tetrahedron, the tetrahedron will experience a distortion and the center of gravity of the negative charges will no longer coincide with the position of the positive central atom, an electric dipole is generated. If all of the tetrahedral in the crystal have the same orientation or some other mutual orientation that does not allow for a cancellation among the dipoles, the crystal will have a macroscopic dipole. The two opposite faces of the crystal have opposite electric charges.

1.3.3 Working principle

The working principle of the touch sensor lies in the coupling of piezoelectric and semiconducting properties. The two metals of the electrodes and ZnO nanowires of the semiconductor make a Schottky barrier. A Schottky barrier is a potential energy barrier for electrons formed at a metal-semiconductor junction. A Schottky barrier has rectifying characteristics. When pressure is applied to the nano-generator, the nanowires are under uniaxial compression and electrons will flow from the tip to the bottom through the external circuit. However, the Schottky barrier obstructs the electrons from passing through the interface. These electrons are blocked and accumulate around the bottom of the nanowires until removing external pressure. During this process, the flow of electrons via the external circuit is detected as an electric pulse. When the external force is removed and the compressive is released, the electrons flow back via the external circuit, creating an electric pulse in the opposite direction. The role of the Schottky barrier is to prevent those mobile charges from passing through the nanowire-metal contact interface. The piezoelectric potential acts as a ‘charging pump’ that drives the electrons to flow. The output voltage of a single nanowire is linearly proportional to the magnitude of its deformation. Therefore, if the pressing force is increased on the nanowires, their deformation becomes larger, and the output voltage will linearly scale up [26] [27].



(a) (b) (c) (d)

Figure 1.11 A mechanism for power generation in. (a) The touch sensor with no external pressure. (b) Electrons flow from the top electrode to the bottom side through the external circuit by the negative piezoelectric potential generated at the top side of the ZnO nanowires under direct compression by the external pressure. (c) The potential is kept since the Schottky contact hinders the electrons from being transported through the interface. (d) The piezoelectric potential dissipates when the external pressure on the top electrode is removed. Electrons flow back via the external circuit.

1.3.4 Synthesis of aligned nanowires

1.3.4.1 Vapor-liquid-solid growth

VLS crystal growth mechanism has been widely used for semiconductor nanowire growth, oxide nanowire growth through the VLS mechanism could be complicated by the presence of oxygen. The process involves the reduction of ZnO powder by carbon to form Zn and CO/CO_2 vapor in the high-temperature zone [20]. Aligned growth of nanowires can be achieved with the use of substrates and catalyst particles or seeds. The large-scale perfect vertical alignment of ZnO nanowires has been firstly demonstrated on a-plane ((11$\bar{2}$0) crystal surface) orientated single-crystal aluminum oxide (sapphire) substrate [21]. Gold seeds were used as catalysts. The growth is initiated and guided by the Au particle and the epitaxial relationship between ZnO and Al_2O_3 leads to the alignment.

$$ZnO(s)+C(s)\leftrightarrow Zn(v)+CO(v)$$

The above reaction is reversible in a relatively lower temperature. So when the Zn vapor and CO were transferred to the substrate region, they could react and became back to ZnO, which could be absorbed by gold catalyst and eventually formed ZnO nanowires through VLS process.

Aligned ZnO nanowires have been successfully grown on sapphire, GaN, AlGaN and AlN substrates [22] through a VLS process, where the crystal structure of substrate is crucial for the orientation of nanowires. Epitaxial relationship between the substrate surface and ZnO nanowires determines whether there will be an aligned growth and how well the alignment can be. The successful alignment of ZnO nanowires on sapphire and nitride substrates is attributed to the very small lattice mismatches between the substrates and ZnO. In the case of sapphire, $(11\bar{2}0)$ plane orientated substrate is always used because the smallest lattice mismatch is along the c-axis of Al_2O_3 and a-axis of ZnO. The epitaxial relationship between ZnO nanowire and a-plane sapphire substrate are $(0001)_{ZnO}||(11\bar{2}0)_{Al2O3}$, $[11\bar{2}0]_{ZnO}||[0001]_{AlO3}$. The lattice mismatch between $4[01\bar{1}0]_{ZnO}(4\times3.2149=12.996Å)$ and $[0001]_{Al2O3}$ (12.99 Å) is almost zero, which confined the growth orientation of ZnO nanowires. Nevertheless, since the $(11\bar{2}0)$ plane of Al_2O_3 is rectangular lattice but the (0001) plane of ZnO is a hexagonal lattice, this epitaxial relationship can only hold in one direction [10].

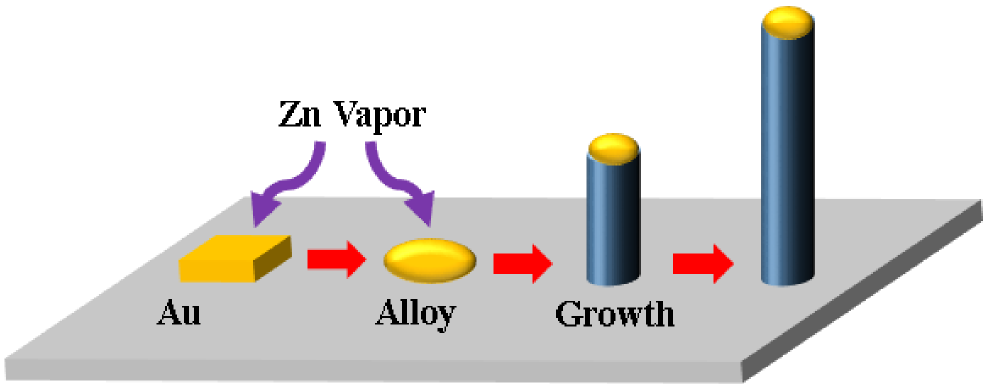


Figure 1.12 Schematic representation of ZnO nanowire growth mechanism.[20]

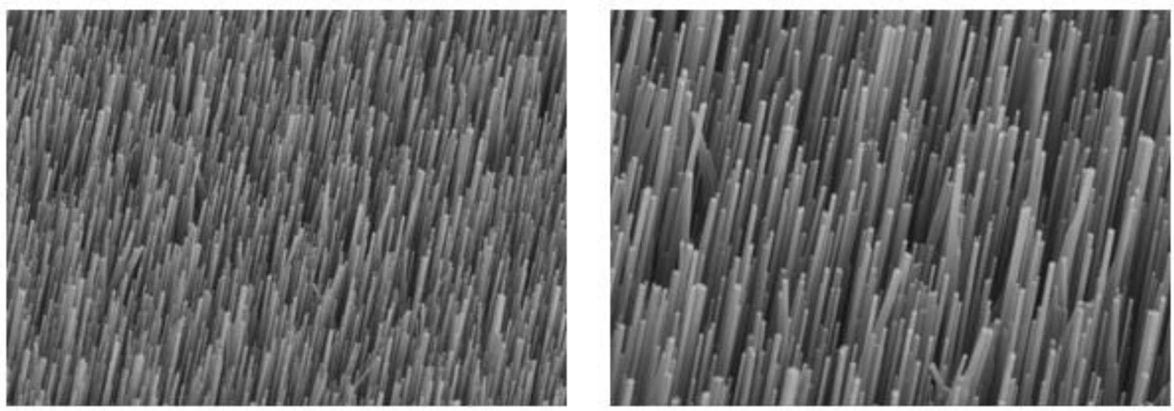


Figure 1.13 ZnO nanowires grown by vapor-liquid-solid process.

1.3.4.2 Hydrothermal based chemical approach

Under specific growth conditions, a wide range of morphologies of ZnO nanostructure have been synthesized. Hydrothermal synthesis is a good approach for synthesis of ZnO nanowires with the use of ZnO seeds in the forms of thin films [23], [24]. By adjusting the precursor concentration, the density of ZnO nanowires arrays could be controlled within one order of magnitude with one nanowire growing from one spot site. The nutrient solution was composed of a 1:1 ration of zinc nitrate and hexamethylenetetramine (HMTA) at low temperature. Zinc nitrate salt provides Zn^{2+} ions required for building up ZnO nanowires. Water molecules in the solution provide O^{2-} ions. Even though the exact function of

HMTA during the ZnO nanowire growth is still unclear, it is believed to act as a weak base, which would slowly hydrolyze in the water solution and gradually produce OH^-. This is critical in the synthesis process because, if the HMTA hydrolyzes very fast and produces a lot of OH^- in a short period of time, the Zn^{2+} ions in solution would precipitate out very quickly due to the high pH environment, which would have little contribution to the ZnO nanowire oriented growth, and eventually results in fast consumption of the nutrient and prohibits further growth of ZnO nanowires.

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 4NH_3 + 6HCHO$$

$$NH_3 + H_2O \leftrightarrow NH_3 \cdot H_2O$$

$$NH_3 \cdot H_2O \leftrightarrow NH_4^+ + OH^-$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

The growth process of ZnO NWs can be controlled through the five chemical reactions listed above. All of the five reactions are actually in equilibrium and can be controlled by adjusting the reaction parameters such as precursor concentration, growth temperature and growth time [10].

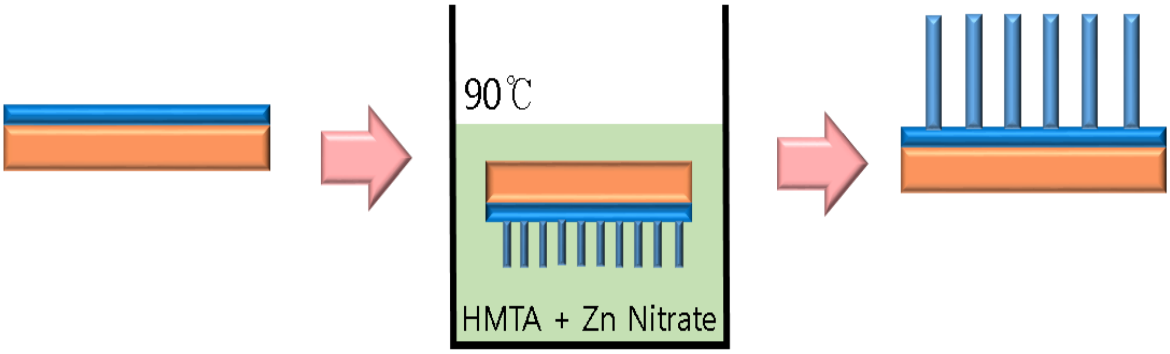
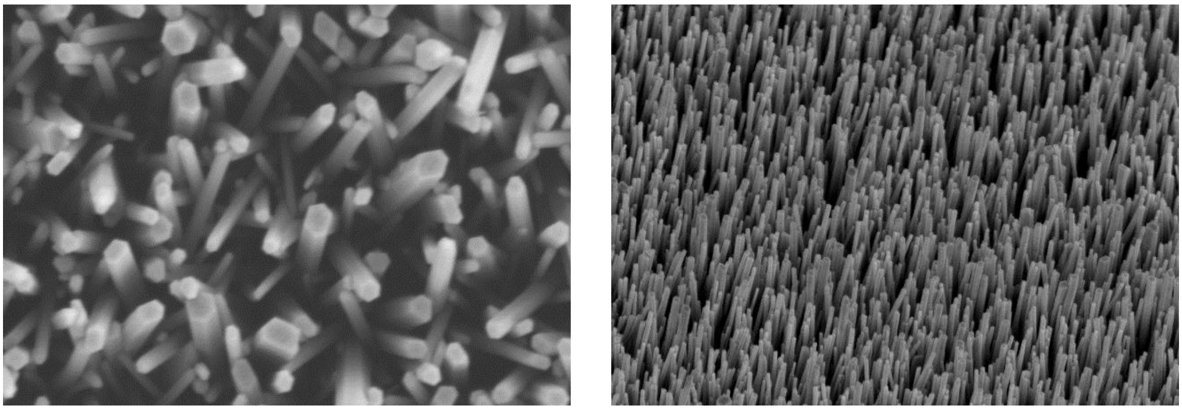


Figure 1.14 A mechanism of hydrothermal synthesis.



(a) (b)

Figure1.15 ZnO nanowires grown by hydrothermal method. (a) Topview. (b) 45° tilted view.

II. Device structure and fabrication

2.1 Device structure

The concept of our novel touch sensor is to design tiny touch sensor arrays similar to the dimensions of a human cell. The tiny touch sensors are composed of a bottom electrode, ZnO nanowires, and a top electrode [26] [27]. In case of ZnO nanowires, It is fundamental element. Therefore, to find optimized condition, several experiment was carried out to grow ZnO nanowires. In the future, they will have a radio antenna to send electrical signals to a signal processor. The tiny touch sensors on the one substrate should have no effect on each other. Therefore, one substrate is an electric insulator. Several touch sensors will detect temperature while, the others will detect the properties of the object such as hardness, roughness, size, and so on. To be applied to robots or humans, the current substrate should be replaced to a flexible plastic substrate [28].

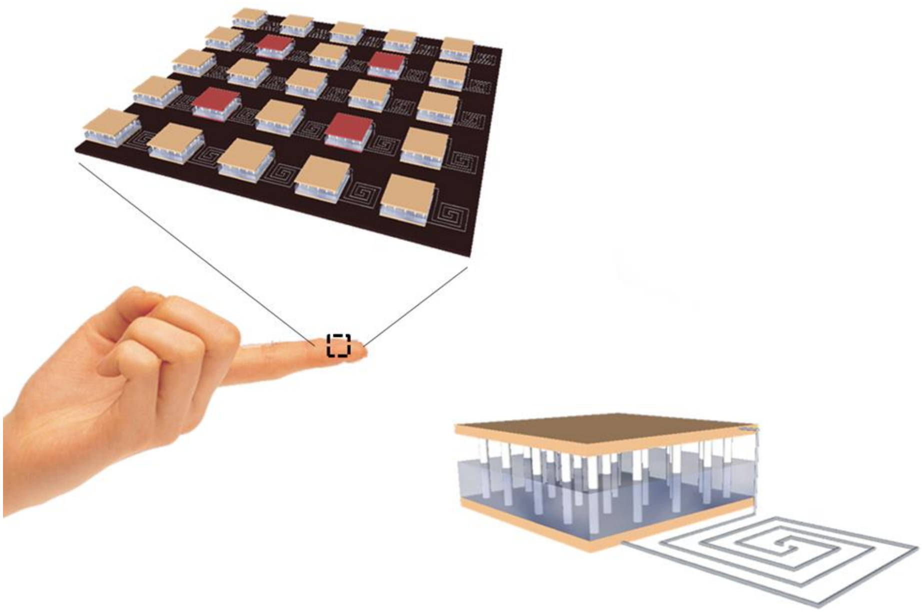


Figure 2.1. A mimetic diagram of touch sensor arrays

2.2 Device Fabrication

2.2.1 Growth of ZnO nanowires by Vapor-Liquid-Solid method

A schematic illustration of the chemical vapor transport and condensation system is shown in Figure 2.2. Sapphire was used as substrates for the ZnO nanowire growth. Firstly, sapphire was cleaned. During the cleaning process, the sapphire was dipped into acetone for 180 seconds and IPA for 60 seconds with ultrasonic agitation. After the cleaning process, the sapphire substrate was coated with a layer of gold thin film using a thermal evaporator to ensure an exact 50 nm of gold film thickness. Equal amounts of ZnO powder and graphite powder were ground together and transferred to an alumina boat. The Au-coated sapphire substrate was also placed near from the ZnO powder and graphite powder on the alumina boat. The boat was then placed inside a furnace quartz tube. The alumina boat positioned at the center of the furnace placed downstream of an argon flow. The temperature of the furnace was ramped to ~800-1000℃ at a rate of ~50-100℃ min^{-1} and typically kept at that temperature for ~5-30 min. After the furnace was cooled to room temperature, light or dark gray material was found on the surface of the substrate [20].

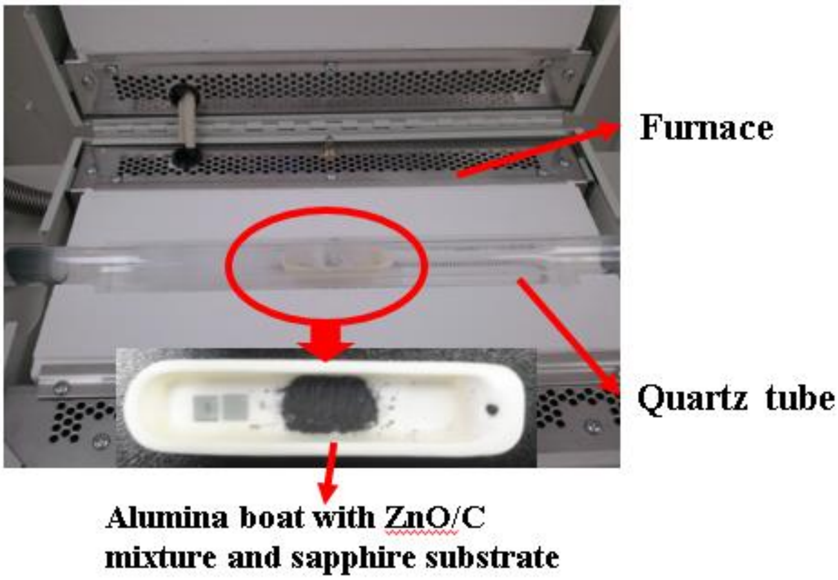


Figure 2.2 the equipment for VLS method

2.2.2 Growth of ZnO nanowires by Hydrothermal method

Hydrothermal method is a good approach for growth of ZnO nanowires with the use of ZnO seeds in the forms of thin films. In this work, we chose silicone (100) and silicone dioxide as the substrates. For simplicity of description, we use silicone substrate to describe the experimental procedure and to illustrate the effects of various experimental parameters on the growth, A piece of silicone (100) wafer substrate was cleaned by a standard cleaning process. First, the wafer was ultrasonicated consecutively in acetone, IPA. Then it was blown dry with nitrogen gas. After cleaning process, a 50 nm thick layer of ZnO was deposited on top of the silicon wafer by RF sputtering system. The next step was to prepare the nutrient solution. The nutrient solution was composed of a 20mMol/900mL 1:1 ratio of zinc nitrate and hexamethylenetetramine (HMTA). The substrate with ZnO seed layer was stuck in a Teflon zig, the Teflon zig fixes the samples to protect the sample from falling. The Teflon with the sample was placed inside a bottle filled with 600mL of nutrient solution. The bottle was placed inside an oven at a temperature of 90℃ for 24 hours. After 48 hours, the sample was removed and cleaned by IPA. Then it was blown dry with nitrogen gas.

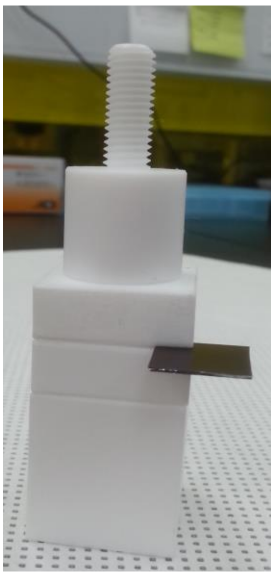


Figure 2.3 Teflon zig with sample

2.2.3 Simple structure fabrication

To know what metal is suitable for the bottom electrode that is an important factor for making a Schottky barrier between metal and the ZnO nanowire of the touch sensor, niobium, nickel and gold were used for comparison. Firstly, Si/SiO_2 (1000Å) was split as 1.5 cm by 1.5 cm and cleaning process was carried out. During the cleaning process, the Si/SiO_2 substrate was dipped into acetone for 180 seconds and IPA for 60 seconds with ultrasonic agitation sequentially. After the cleaning process, spin coating was carried out with Ma-N1420 negative photoresist (PR) onto the Si/SiO_2 substrate. A rotation speed of 4000 rpm was used to get approximately 1um of thickness of the photoresist. Then, a soft bake was performed at 100℃ for 120 seconds on a hot plate. A piece of the substrate was irradiated with $40mJ/cm^2$ of UV from a mercury lamp. The exposed piece was submerged into Ma-D 533 S developer for approximately 60 seconds. Through this process, the partial photoresist disappeared and all samples had the same area having a height of 1.2 cm and a width of 1 cm for making position of bottom electrode with different metals. The RF sputtering system was used to deposit metals such as niobium (100nm), nickel (50nm), and gold (50nm) onto the Si/SiO_2/patterned photoresist substrate. After metal deposition, the lift-off was carried out with acetone to remove photoresist and obtain a final bottom electrode. To deposit a ZnO layer, the above process of spin coating the photoresist to lift-off were repeated with an align technique of UV photolithography step to make area of 1cm by 1cm on the bottom electrode exactly. These three kinds of samples were stuck in a Teflon zig. Teflon fixes the sample to protect the sample from falling. The Teflon with the sample was placed inside a bottle filled with nutrient solution. The nutrient solution was composed of a 20mMol/900mL 1:1 ratio of zinc nitrate and hexamethylenetetramine (HMTA). And then, the bottle was placed inside an oven at a temperature of 90℃ for 48 hours. After 48 hours, the sample was removed and cleaned by IPA. Finally, an ITO glass was placed on the fabricated simple structure. Then, the top electrode and bottom electrode were attached wire by using silver paste.

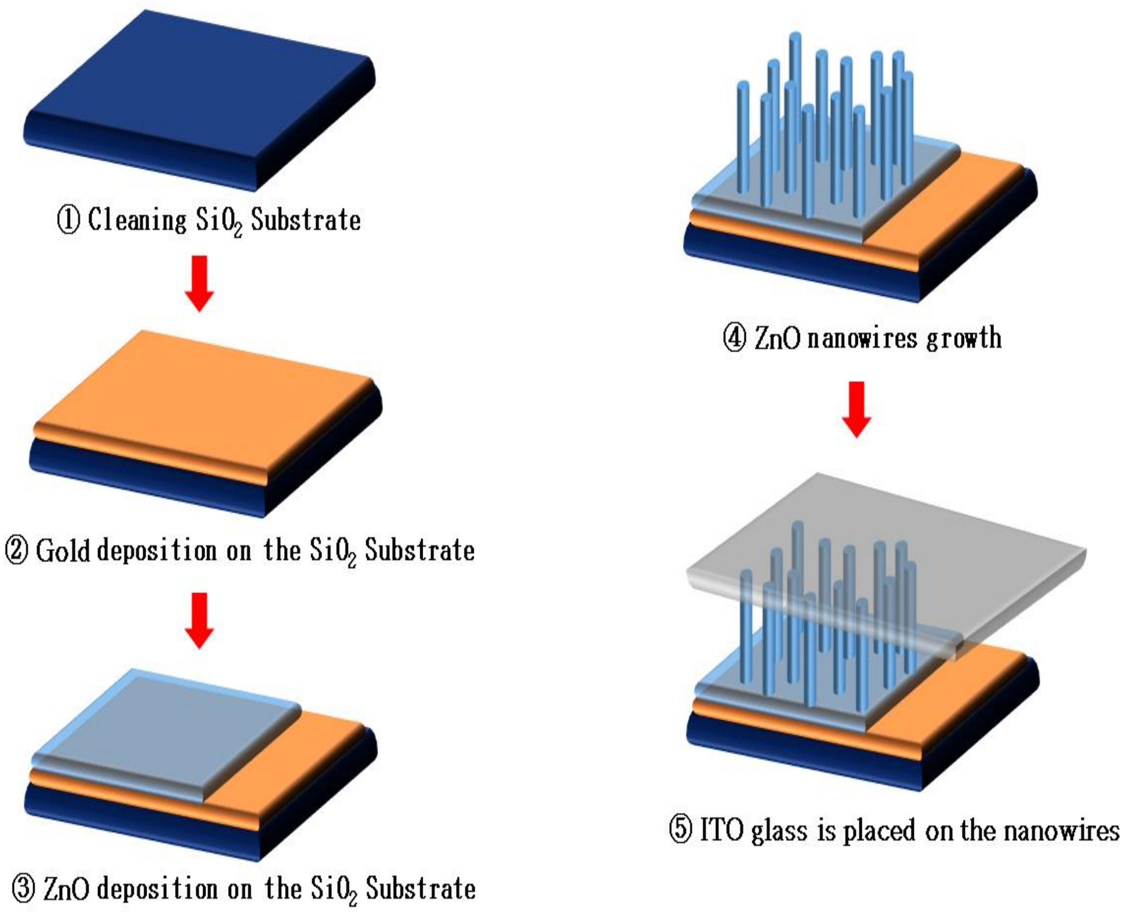


Figure 2.4 A mechanism of simple structure fabrication

2.2.4 Segment structure fabrication

Because a concept of this research is to design arrays similar to the size of a human cell, a small size basic structure was fabricated on one substrate. They are fabricated on Si/SiO_2 (1000Å) to prevent the devices from unexpected leakage current that leads to low performance. The segment type is a 3 by 3 square pattern measuring 2mm by 2mm. The patterns were designed by MyCAD and exported to Gerber 2 format to make 5’’ chrome photo-mask. Before starting the fabrication, Si/SiO_2 substrate was split to 2 cm by 2 cm and a cleaning process was carried out. In the cleaning process, the Si/SiO_2 substrate was dipped into acetone for 180 seconds and IPA for 60 seconds with ultrasonic agitation sequentially. After the cleaning process, spin coating was carried out with an AZ GXR-601 positive photoresist onto the Si/SiO_2 substrate to make a 3 by 3 square pattern. A rotation speed of 1500 rpm was used to get approximately 1.5 um of thickness of the photoresist. Then, a soft bake was performed at 100℃ for 120 seconds on a hot plate. The substrate was exposed to $40mJ/cm^2$ of UV from a mercury lamp. The exposed piece of wafer was dipped into AZ 300 MIF developer for approximately 60 seconds. The 50 nm of gold was deposited onto the 3 by 3 patterns by RF sputtering system because it was confirmed that gold is suitable for bottom electrode through prior experiment with simple structure. Then, the lift-off was carried out with acetone to remove any photoresist. To deposit a ZnO layer, the process of spin coating with an AZ GXR-601 positive photoresist was repeated. Then, the substrate was carried out with align technique of UV photolithography step. The exposed piece of wafer was dipped into AZ 300 MIF developer for 60 seconds, and the ZnO was deposited by RF sputtering system. The ZnO layer position size was height and width of 1.2 cm and covered with 3 by 3 gold patterns. This prepared sample that was not carried out lift off was stuck in a Teflon zig. Teflon fixes the sample to protect the sample from falling. The Teflon with the sample was placed inside a bottle filled with nutrient solution. The nutrient solution was composed of a 20mMol/900mL 1:1 ratio of zinc nitrate and hexamethylenetetramine (HMTA). And then, the bottle was placed inside an oven at a temperature of 90℃ for 48 hours. After 48 hours, the sample was removed and cleaned by IPA. Then, the lift-off was carried out with acetone to remove photoresist and residuals of ZnO nanowires. Finally, an ITO glass was placed on the fabricated simple structure. Then, the top electrode and bottom electrode were attached wire by using silver paste.

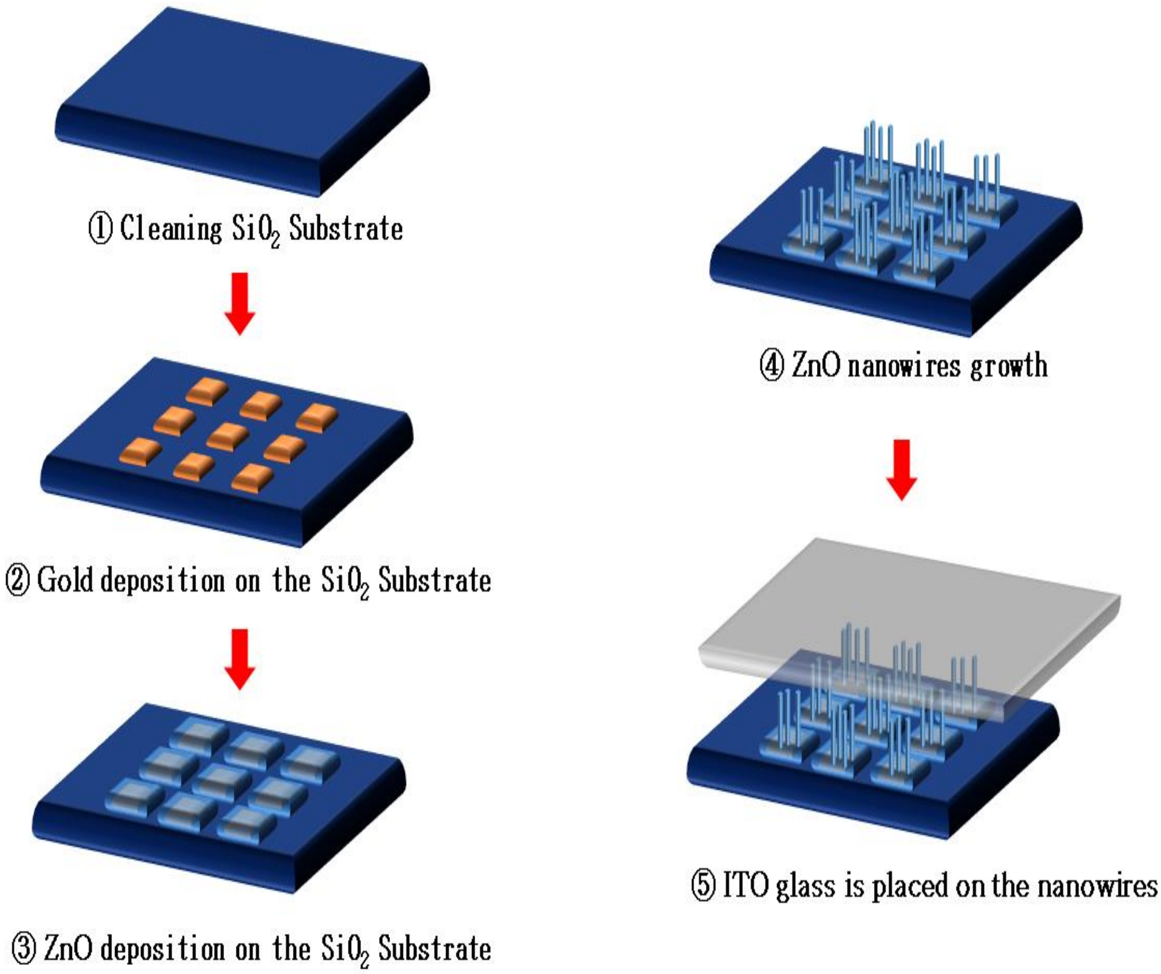


Figure 2.5 A mechanism of the segment structure fabrication

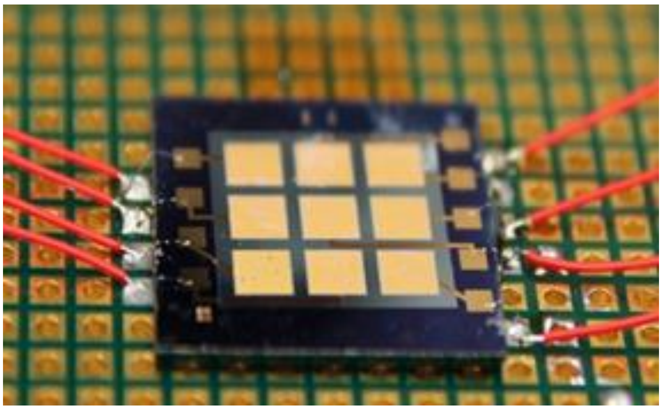


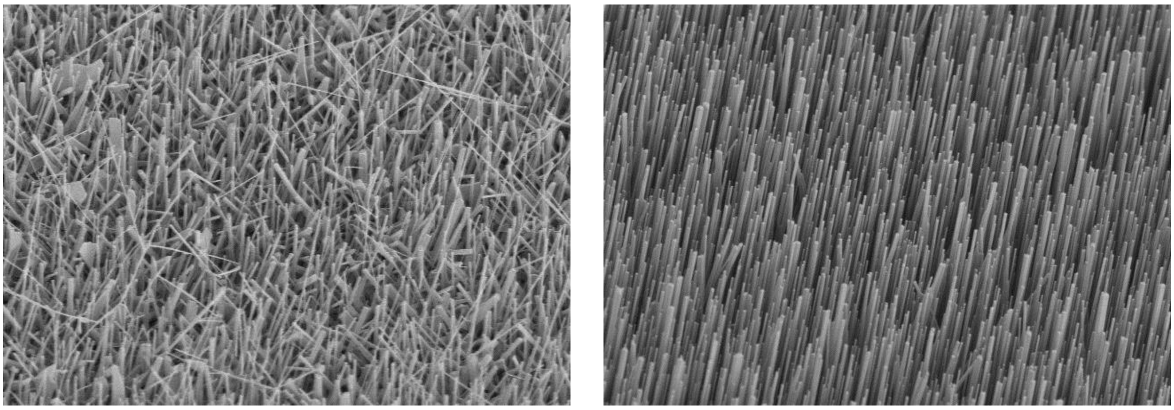
Figure 2.5 A fabricated 3-by-3 segment structure device

III. Result and Discussion

3.1 Vapor-Liquid-Solid growth

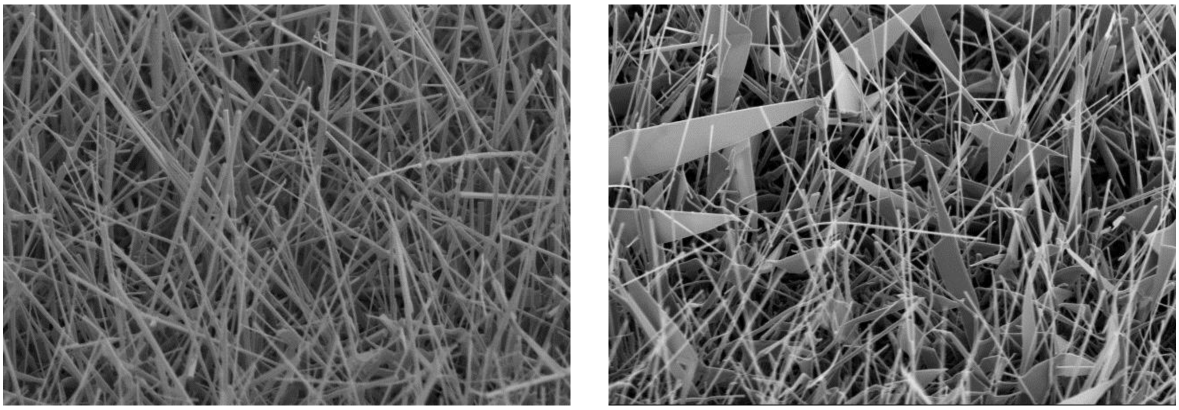
Vapor-Liquid-Solid method usually requires single-crystal substrates and high operation temperature. Firstly, sapphire was used as a substrate. To grow ZnO nanowires vertically, the constant flow of argon and furnace temperature were controlled. Also, the position of sapphire substrate was an important factor for growth of vertical ZnO nanowires. As shown in Figure 3.1, the ZnO nanowires showed different verticality with different gas flow. In this experiment, when the temperature was 910℃, proper argon gas flow which is required for growing vertical ZnO nanowires, was 12sccm.

Secondly, silicon dioxide, a non-single-crystal, was used as substrate as shown in Figure 3.2. The best conditions such as furnace temperature, thickness of gold catalyst, and argon gas flow were applied to grow ZnO nanowires. The conditions were conducted using sapphire substrate. However, the result was completely different. Although ZnO nanowires were thin and long, several chips developed around the ZnO nanowires, and it looked messy. From these results, we could find the probability to control growing ZnO nano wires by changing the conditions such as the ratio of a gas flow, temperature, and a position of substrate. Also, sapphire was a good substrate to grow vertical ZnO nanowires. However, this research required a growth process with low temperature because flexible substrate such as plastic and polymer cannot endure high temperatures. Although the VLS method made thin ZnO nanowires vertically, they were unsuitable to grow ZnO nanowires because the Vapor-Liquid-solid method requires single-crystal substrates and high temperatures, which are expensive and incompatible with plastic substrates for applications in flexible and wearable electronics.



(a) (b)

Figure 3.1 SEM images of ZnO nanowires grown on the sapphire. (a) Furnace temperature was 910℃, and argon gas flow was 10sccm. (b) Furnace temperature was 910℃, and argon gas flow was 12sccm.

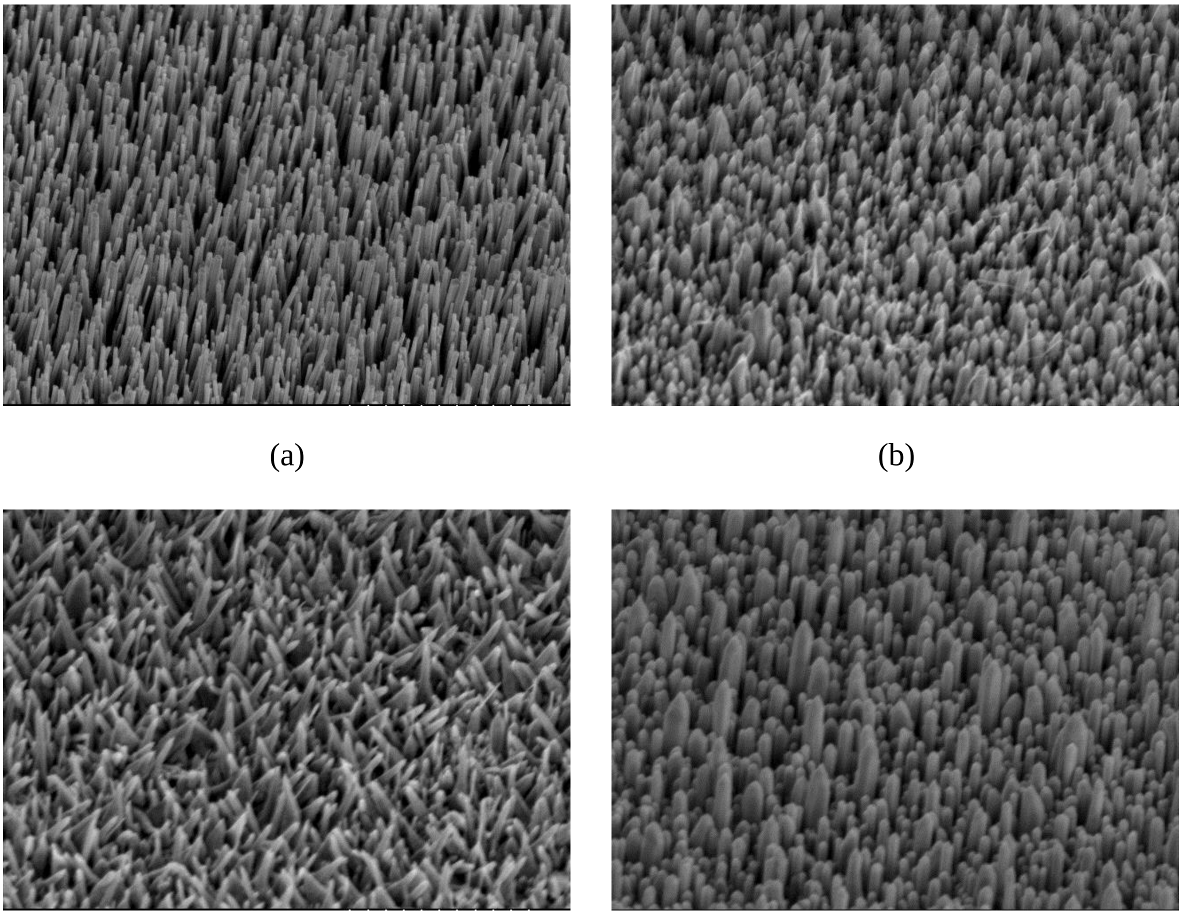


(a) (b)

Figure 3.2 SEM images of ZnO nanowires grown on the silicon dioxide substrate. (a) Furnace temperature was 910℃, and argon gas flow was 12sccm. (b) The silicon dioxide was coated niobium. Then, gold catalyst was coated. Furnace temperature was 910℃, and argon gas flow was 12sccm.

3.2 Hydrothermal growth

As mentioned above, the VLS method usually requires single-crystal substrates and a high operation temperature, both of which are expensive and incompatible with plastic substrates for applications in flexible and wearable electronics. On the contrary, the hydrothermal method is a good alternative approach. The growth temperature can be as low as 80-100℃. As a result, many kinds of substrates, including amorphous oxide on silicon,



(c) (d)

Figure 3.3 SEM images of ZnO nanowires with different conditions. (a) ZnO nanowires grown on the silicon substrate without any treatment. (b) ZnO seed was deposited at room temperature of 20℃, and annealing process was applied at 600℃. (c) ZnO seed was deposited at temperature of 300℃, and annealing process was applied at 600℃. (d) ZnO seed was deposited at temperature of 600℃, and annealing process was not applied.

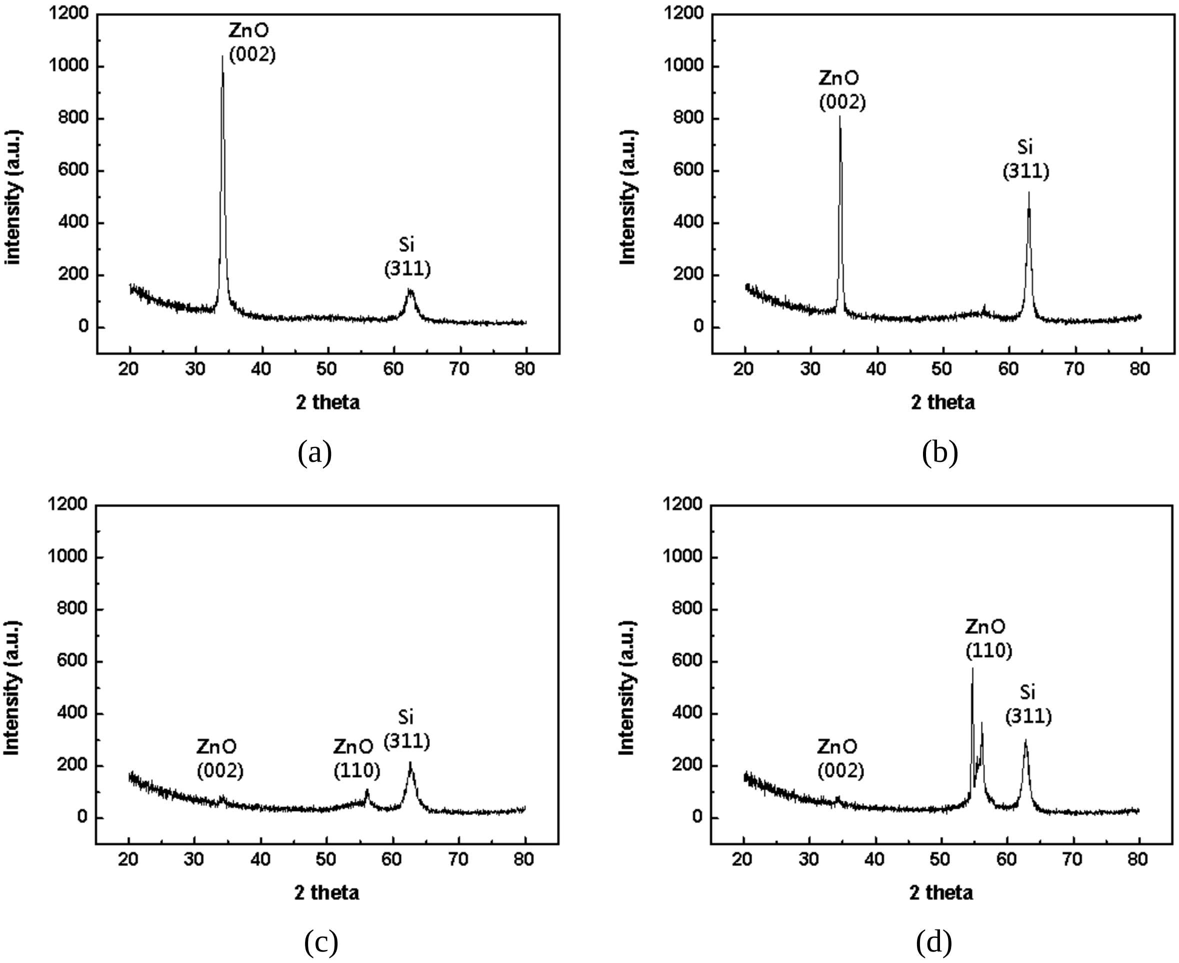
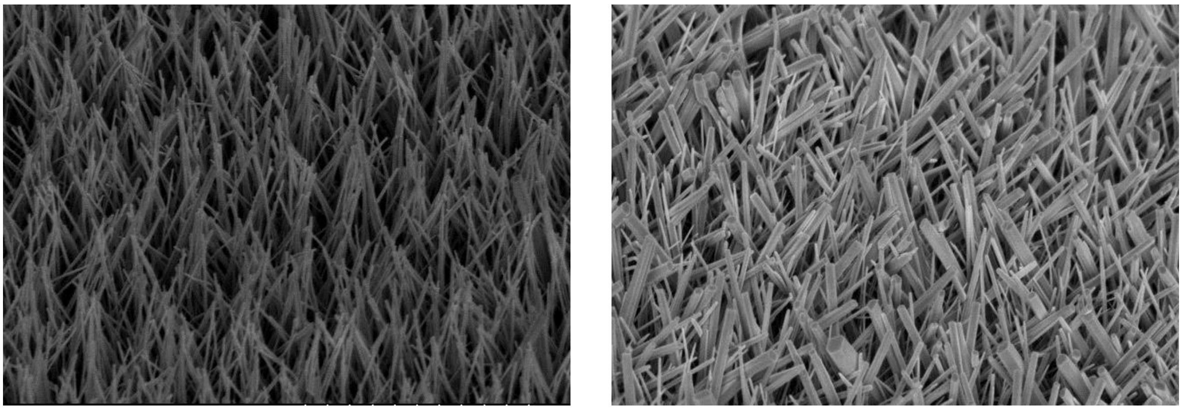


Figure 3.4 X-ray diffraction spectra of ZnO nanowires prepared at different conditions. (a) There is no any treatment. (b) ZnO seed was deposited at room temperature of 20°C, and annealing process was applied at 600°C. (c) ZnO seed was deposited at temperature of 300°C, and annealing process was applied at 600°C. (d) ZnO seed was deposited at temperature of 600°C, and annealing process was not applied.

glass, and polymers, can be employed. In this experiment, ZnO nanowires were grown on the on the silicon substrate. Basically, when ZnO seed was deposited, the deposition temperature was 20°C, and process annealing did not occur. However, they showed different properties with their growth conditions, as shown in Figure 3.3. The deposition temperature of ZnO seed and process annealing after ZnO seed deposition affected the shape, thickness, length, verticality, and so on. When several results such as morphology and thickness were compared, the ZnO nanowires on just the silicon were suitable for this research. As shown in Figure 3.4, XRD spectra also proved the results of experiment. The intensity peak of ZnO on just silicon without any treatment is the highest, and it means the crystallinity of ZnO is better than others. The kinds of substrate also affected the growth of ZnO nanowires. In Figure 3.5, each ZnO nanowire has a different substrate. The morphology, verticality, and thickness were different with each kind of substrate. When several results such as morphology, verticality, thickness, and so on were compared with substrates, the untreated silicon substrate shows well-aligned and well-separated ZnO nanowires. From this experiment, it was confirmed that the growth of ZnO nanowires was affected by kinds of substrate or various conditions. Therefore, because this work requires well-aligned ZnO nanowires, silicon substrate showed the best results. Also, this experiment was confirmed that the properties of ZnO nanowires can be controlled by several conditions.



(a) (b)

Figure 3.5 SEM images of ZnO nanowire with different substrate. (a) ZnO nanowires grown on the silicon dioxide. The silicon dioxide was coated niobium. Then, ZnO seeds was coated on the niobium layer. (b) ZnO nanowires grown on the ITO glass.

3.3 X-Ray Diffraction with conductive layer

Above experiment results showed that ZnO nanowires on the silicon substrate without any treatments was well-aligned. However, silicon is semiconductor to allow electron movement. Therefore, if the touch sensor arrays are fabricated on the silicon substrate, each sensors cannot operate separately. Alternately, silicon dioxide substrate was used, because oxide layer obstructs electron movement. The each touch sensors need respective conductive layers. Therefore, the experiment to know the crystallinity of ZnO nanowires on the several kinds of conductive layer was carried out, and X-Ray Diffraction system was used. The verticality of ZnO nanowires is also important factor to be power generator because vertical ZnO nanowires can generate much more piezopotential than non-vertical ZnO nanowires. X-Ray Diffraction is a useful method to discover the microstructure of some materials. When X-ray interact with a crystalline substance, one gets a diffraction pattern. Every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others. Therefore, the X-ray diffraction pattern of a pure substance is like a fingerprint of the substance. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions we will have destructive interference, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern, and in a very few directions we will have constructive interference. The waves will be in phases and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another [29]. As mentioned about these principles, the crystallinity or verticality of ZnO nanowires were analyzed to find optimized condition. Therefore, if ZnO nanowires on the certain

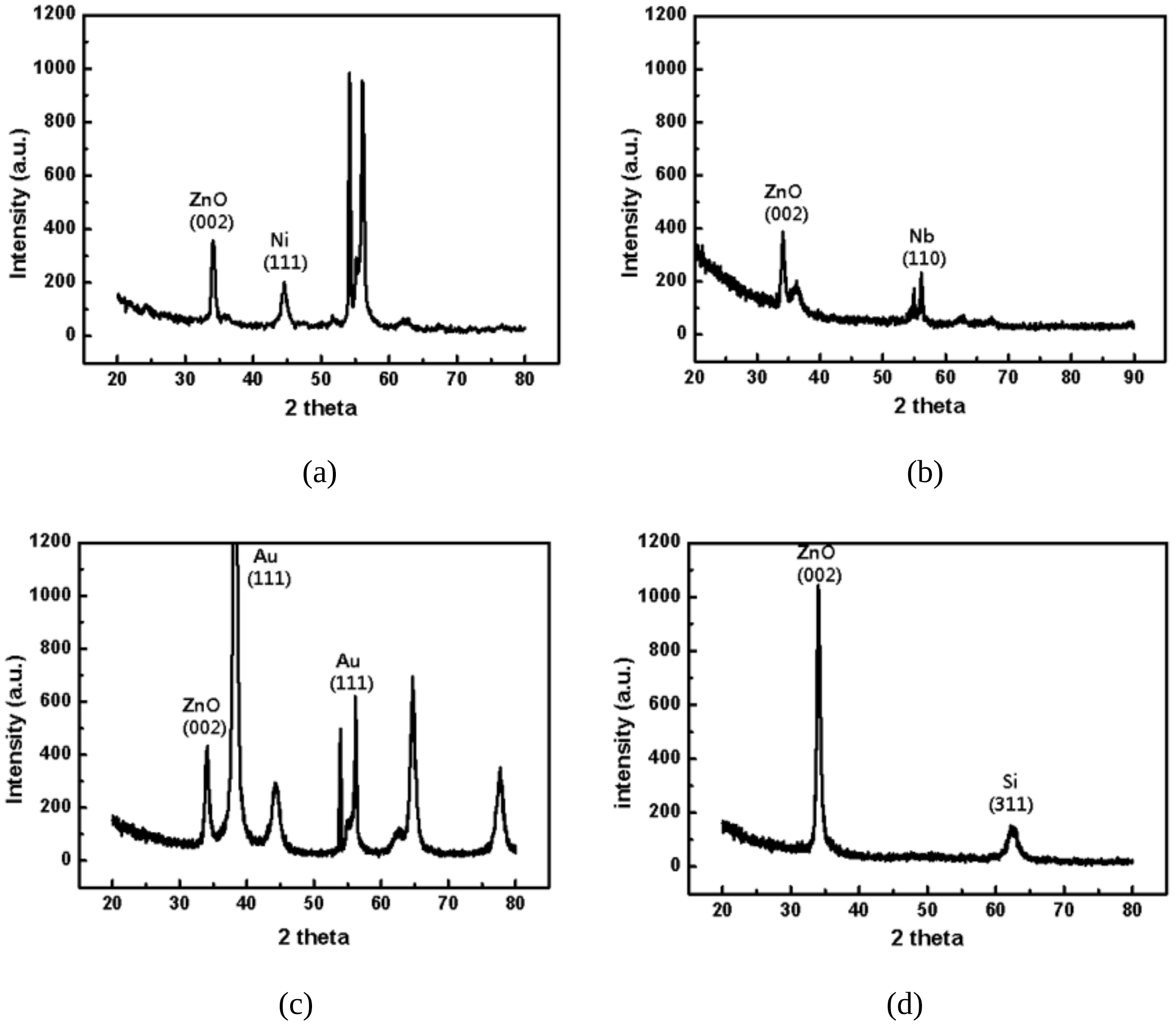
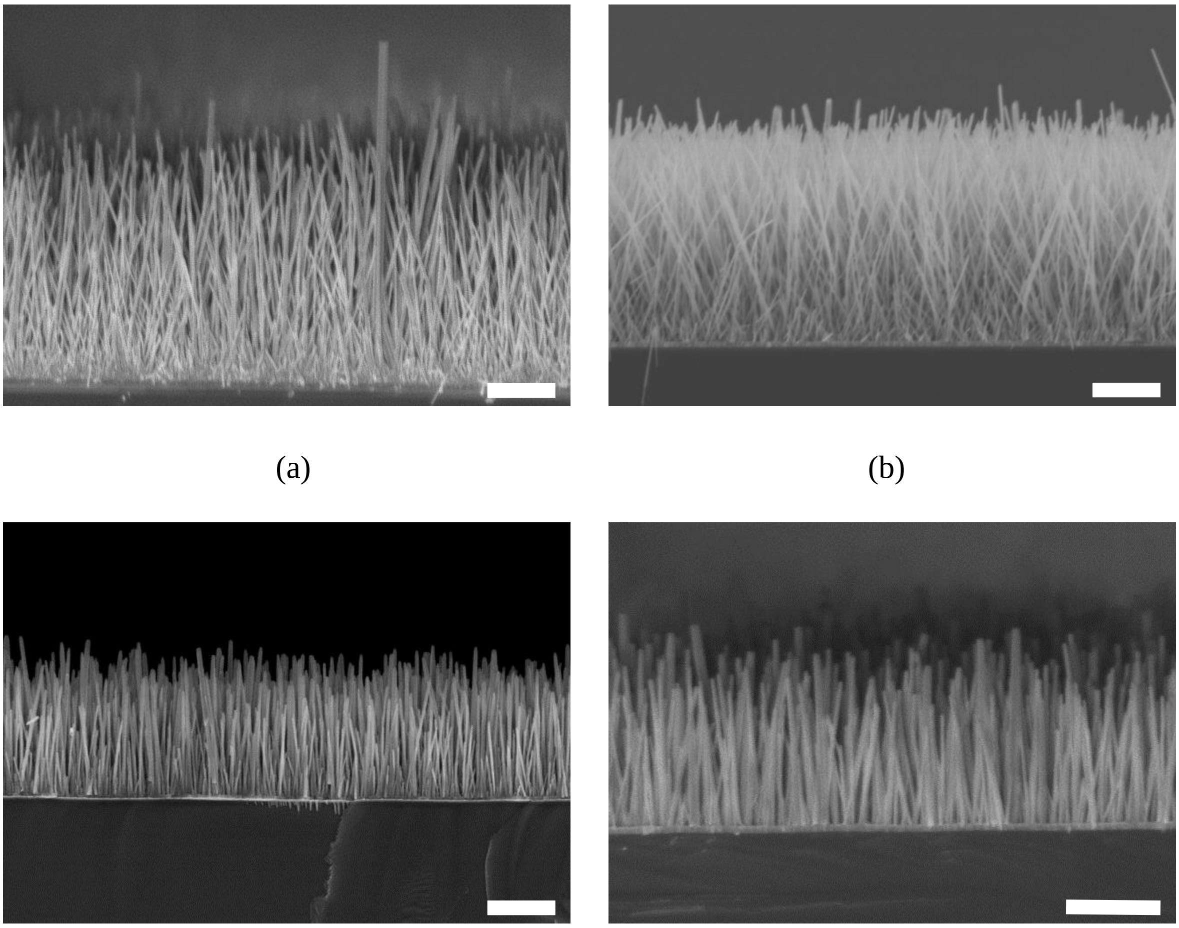


Figure 3.6 The X-ray diffraction graph according to ZnO nanowires on the three kinds of metal and silicone substrate. (a) Niobium (Nb). (b) Nickel (Ni). (c) Gold (Au).(d) silicone (Si)

bottom electrodes have good crystallinity, they make good piezopotential. As shown in Figure 3.6, the X-ray diffraction would shows characteristic high and sharp peaks according to ZnO nanowires on the niobium, nickel, gold layer, and silicon substrate at certain positions in the graph. Theoretically, the peak of ZnO having good crystallinity should be shown in the vicinity of 34°. The Figure 3.6 also shows ZnO peaks in the vicinity of 34°. In the order of Figure 3.5 (a), (b), (c) and (d), the peak of niobium is about 56°, 45° of nickel, and gold is in the vicinity of 38° and 57°. Silicone peak shows in the 63°. In Figure 3.7, the cross view of SEM images shows respective properties with metals of conductive layer.



(a) (b) (c) (d)

Figure 3.7 The SEM images of ZnO nanowires with conductive layer. The metals of conductive layer are (a) niobium, (b) nickel, (c) gold, and (d) silicon substrate. (The scale bar is correspond to 1um)

The most important is ZnO peak, because we should know what metal is suitable for bottom conductive layer. All occasions of the ZnO peak are compared, they do not have a big gap except in the case of silicone. Although the ZnO nanowires on the silicone substrate showed a highest peaks in the graph, silicone could not be suitable. If touch sensors are fabricated on the silicone substrate, they cannot be operated respectively. The silicone substrate cannot prevent the devices from unexpected leakage current because electrons can act move the silicone, and it leads to low performance. Alternatively, the metal layer is needed to fabricate respective conductive layer on insulator substrate. Therefore, the three kinds of metal was tested. Among them, the ZnO peak on the gold layer shows a peak above 400 higher. That means the crystallinity of ZnO nanowires on the gold layer is better than others, and they can make good piezopotential.

3.4 Power generation

3.4.1 Measurement system

To know the electrical signal properties of ZnO nanowires, a piezo-electric measurement system was made. The system consisted of an XYZ linear position stage, motion actuator, a load cell/digital indicator, and a system control. The principle of the system operation was that a fabricated sample was placed on the position stage, and the motion actuator pressed the sample at a moment. The samples have a top and bottom electrode, and both electrodes had wires attached separately with silver paste. The power and frequency of the motion actuator can be controlled. When the motion actuator was operated, the generated signals were shown through a digital phosphor oscilloscope (Tektronix DPO3034). If the wires of the fabricated sample were directly connected to the probes of the oscilloscope, the generated signals were electric voltage values. In the case of current, a low noise current amplifier SR 570 was used to measure minute electric currents. Therefore, when the current was measured, the wires of the sample were directly connected to the probe of the low noise current amplifier. Then, the low noise current amplifier and oscilloscope were connected by cable. The electric signals should be converted to Ampere units.

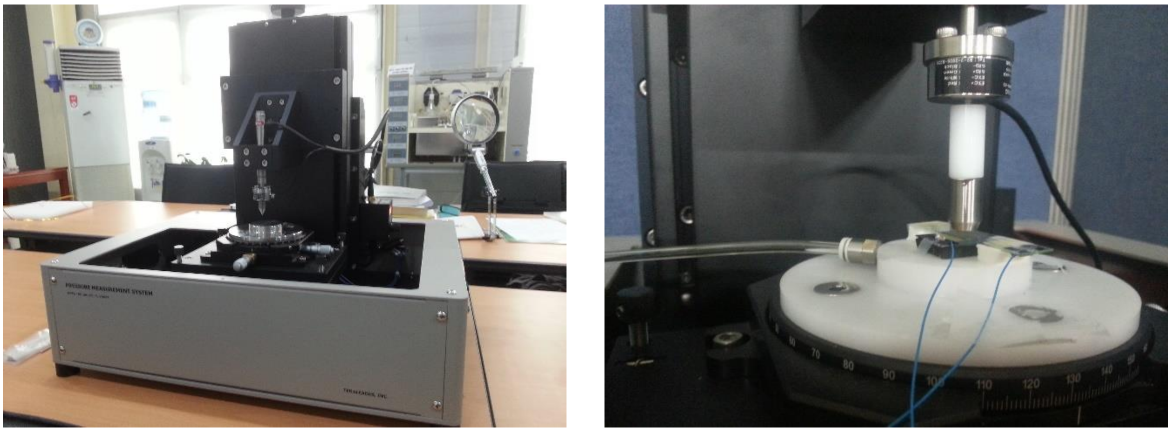
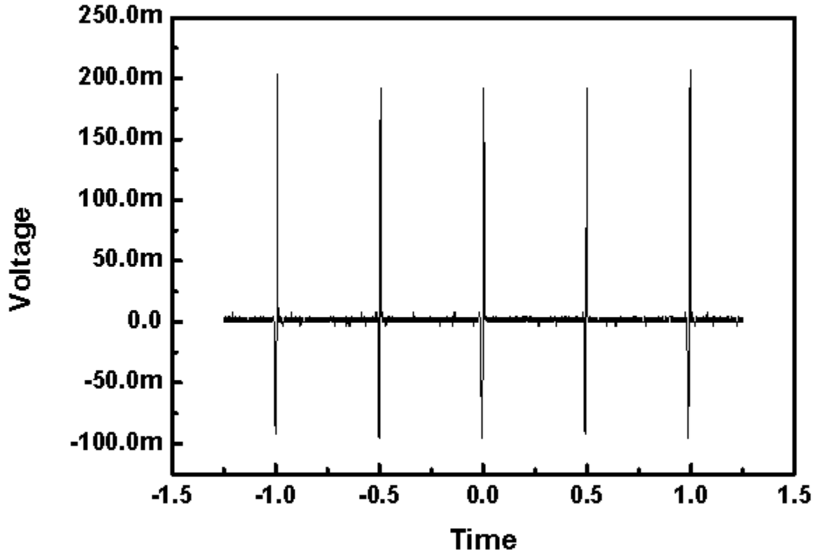


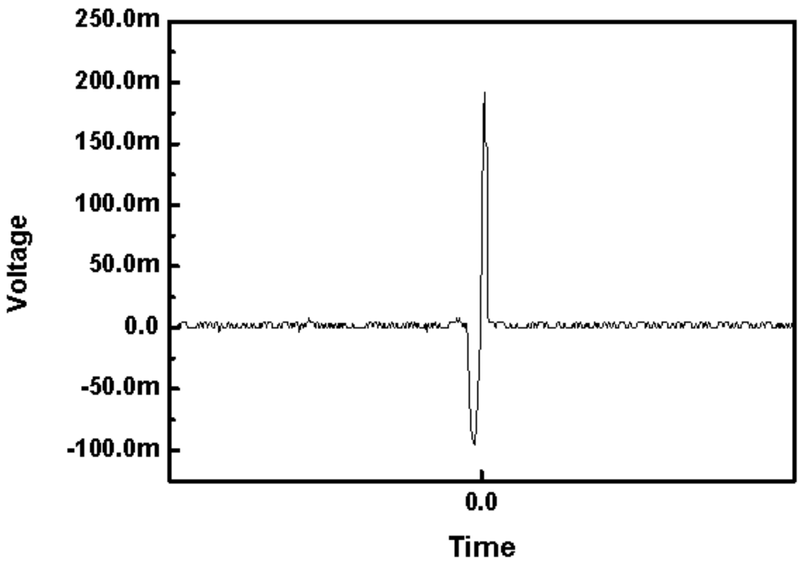
Figure 3.8 The piezoelectric measurement system.

3.4.2 Electrical signals with conductive layer

To know power generation with conductive layer, polarity reversion tests was carried out. The signals were truly from the fabricated devices. As shown in Figure 3.9, when pressure was applied to the device, minus peak was shown. Then, the external force was removed and the compressive strain was released, plus peak was shown. An ITO glass was placed on the fabricated simple structure samples as top electrode in shown Figure 2.4. The samples have different conductive layers such as niobium, nickel, gold, and silicone under the ZnO nanowires. If pressure is applied to the top electrode, the ZnO nanowires between the two electrodes make piezopotential. The Schottky barrier between the bottom electrode and the ZnO nanowires is an important element in devices. The Schottky barrier is different kinds of metal. The generated electrical signals are also affected by Schottky barrier. To measure generated voltage and current, an oscilloscope and low noise current amplifier SR 570 are used. As shown in Figure 3.10(a), when just silicone substrate was used, generated voltage was the highest. However, silicone substrate cannot prevent the devices from unexpected leakage current that leads to low performance. Therefore, the independent conductive layers were needed to be operated touch sensor respectively. In case of current, when the conductive layer is gold, high current value was shown. In the Figure 3.10 (b), Power was combined by voltage and current. It shows that the gold conductive layer as bottom electrode leads to high performance.

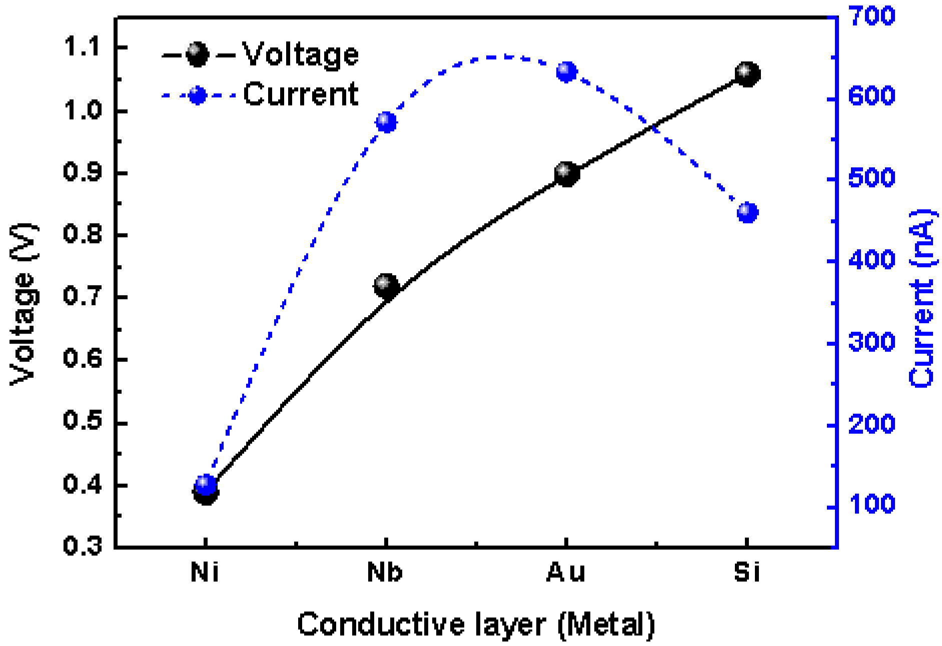


(a)

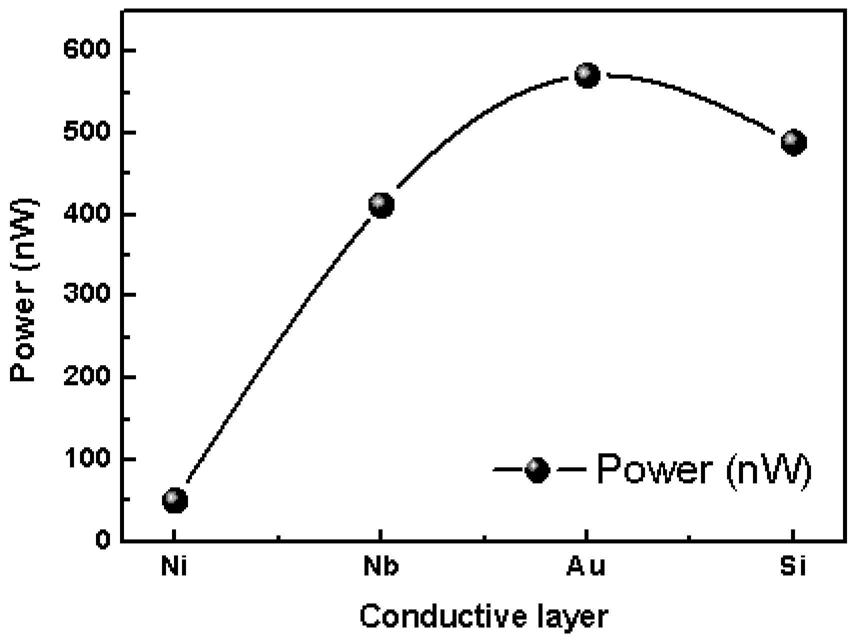


(b)

Figure 3.9 The electrical signals with repeated touching at constant speed and pushing power. (a) When pressure was applied to the device, minus peak was shown. Then, the external force was removed and the compressive strain was released, plus peak was shown. (b) Enlarged electrical signal peak. It shows minus and plus peak, surely.



(a)

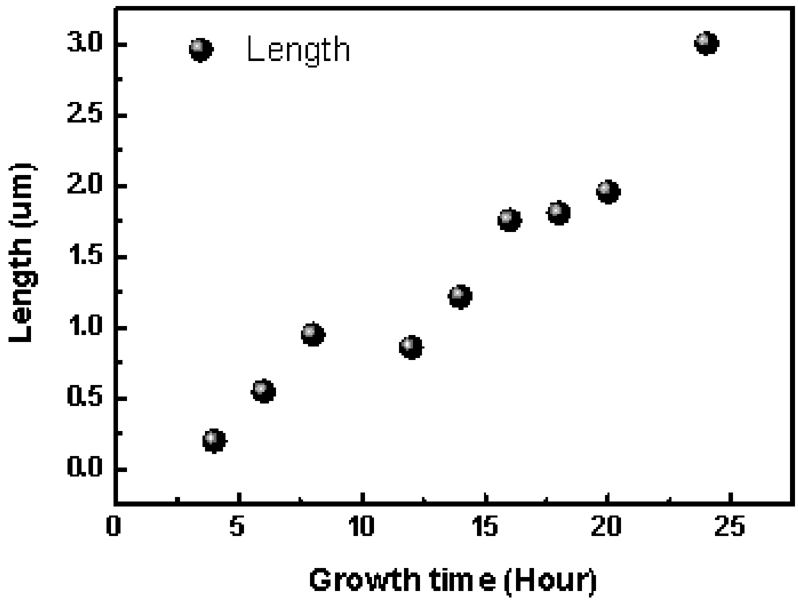


(b)

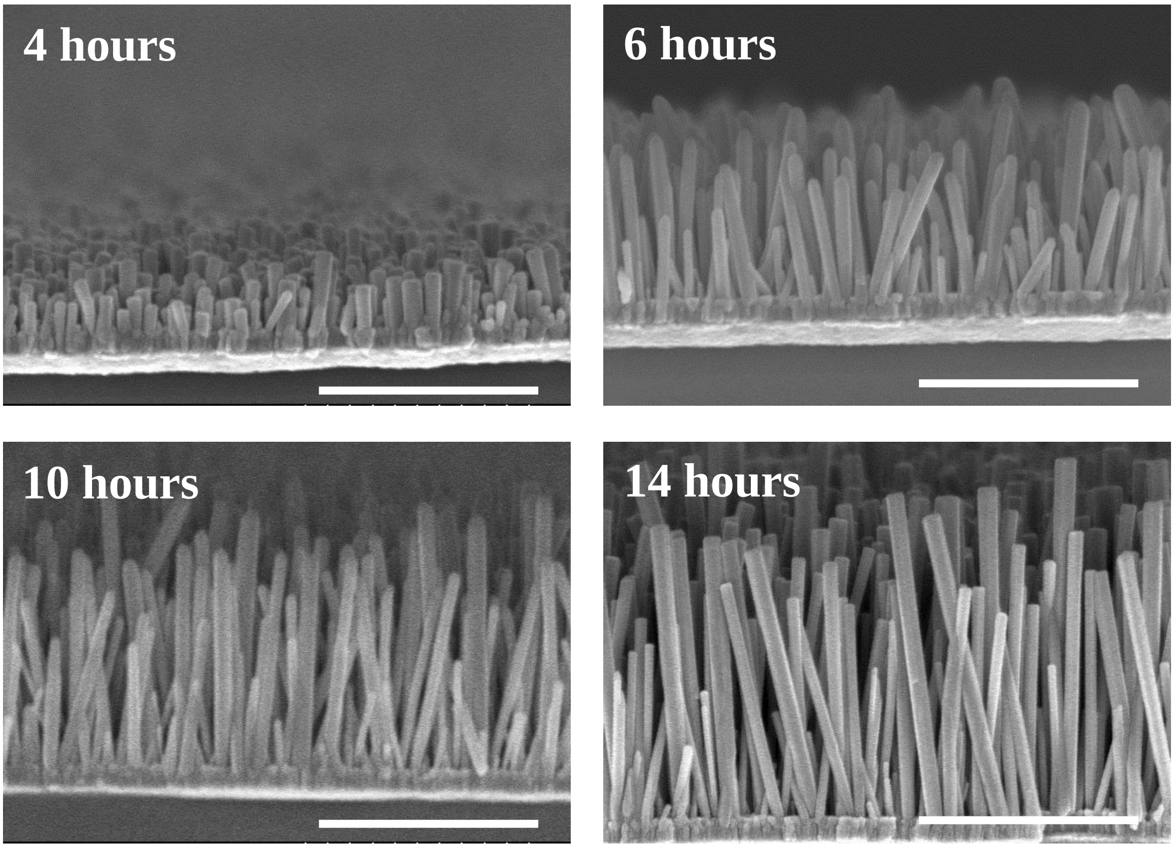
Figure 3.10 The values of electrical signals with conductive layers. (a) Voltage and current according to a kind of conductive layer. (b) Power involved voltage and current according to several conductive layers.

3.4.3 Electrical signals with length of ZnO nanowires

To grow ZnO nanowires, a sample having ZnO seed layer should be dipped into nutrient solution with a 1:1 ratio of zinc nitrate and hexamethylenetetramine (HMTA) at temperature of 90℃. The nutrient solution had a concentration of 20mMol/900mL. The generated electrical signals can be control by a length of ZnO nanowires and an amount of external pressure. As shown in Figure 3.11 (a), the samples were placed inside the bottle with nutrient solution, and they were checked every two hours of growth time. The length of ZnO nanowires are proportional to the growth time. Figure 3.11 (b) shows SEM images of ZnO nanowires with time. The fact that a length is proportional to dipping time was confirmed through SEM images. As show in the Figure 3.12 (a), the voltage and current were measured every two hours of growth time. In case of voltage, the electrical signal was increased from about 80 mV to 150 mV. The current is also increased from 250 nA to 400 nA. It means that the longer the length, the bigger their electrical signals. External pressure also can be a controlling element to change the generated voltage. Figure 3.12 (b) shows that the larger the external pressure, the bigger their electrical signals. From these experiment results, the probability of the best performance was found by controlling a length of ZnO nanowires and external pressure.

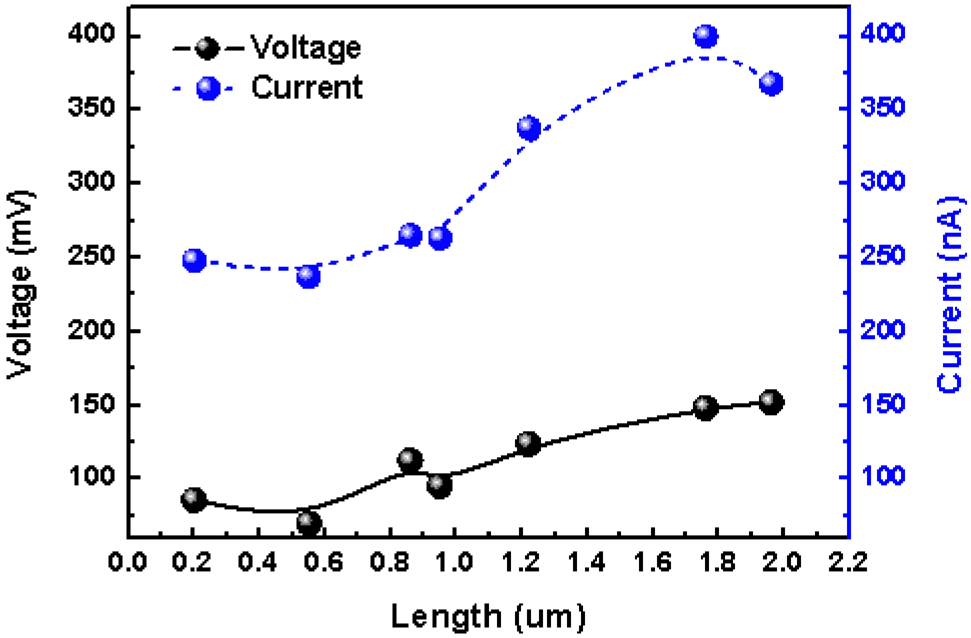


(a)

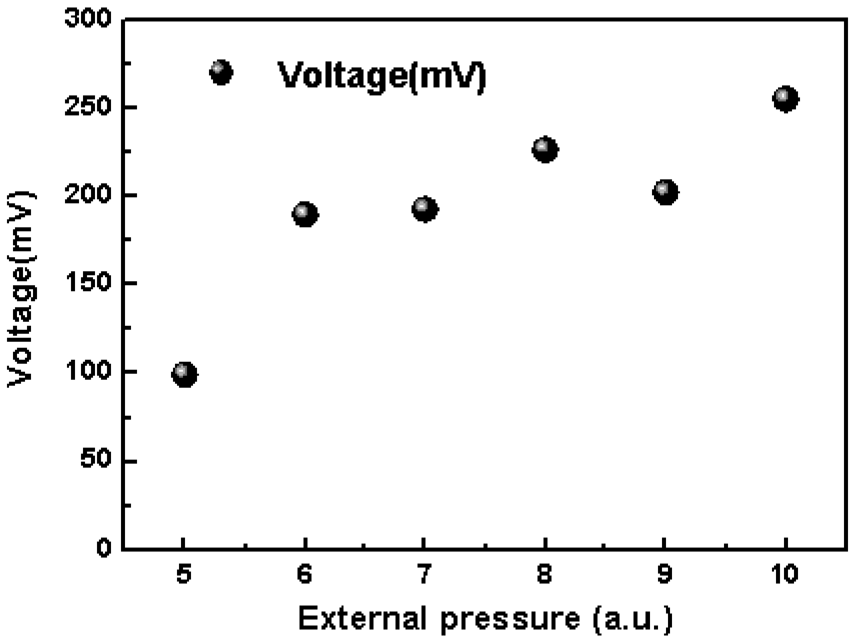


(b)

Figure 3.11 The length of ZnO nanowires with time. (a) The length of ZnO nanowires is proportional to the growth time. (b) SEM images of ZnO nanowires with growth time. (The scale bar is correspond to 1um)



(a)

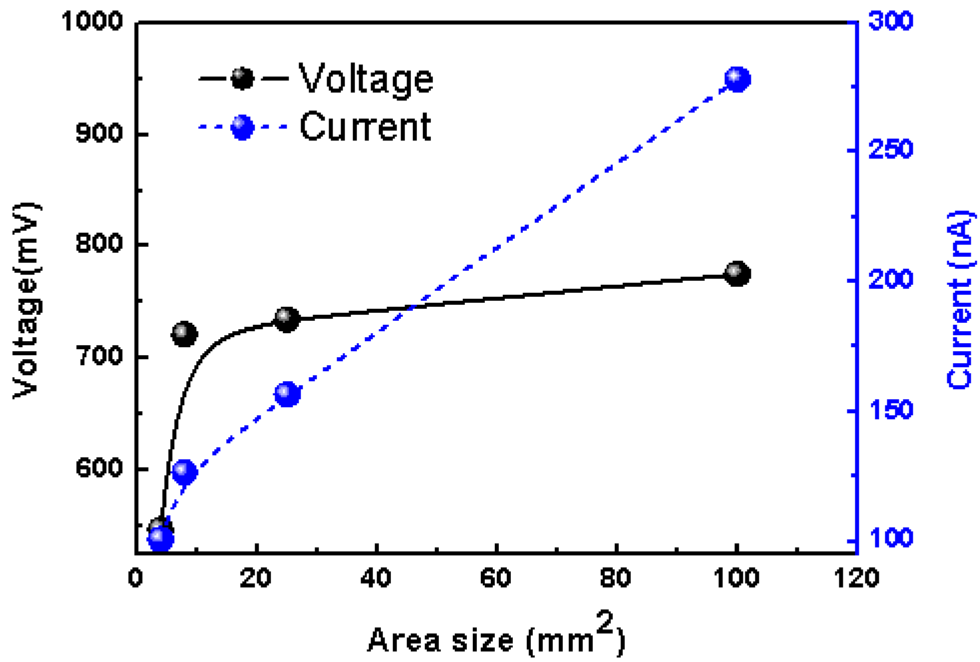


(b)

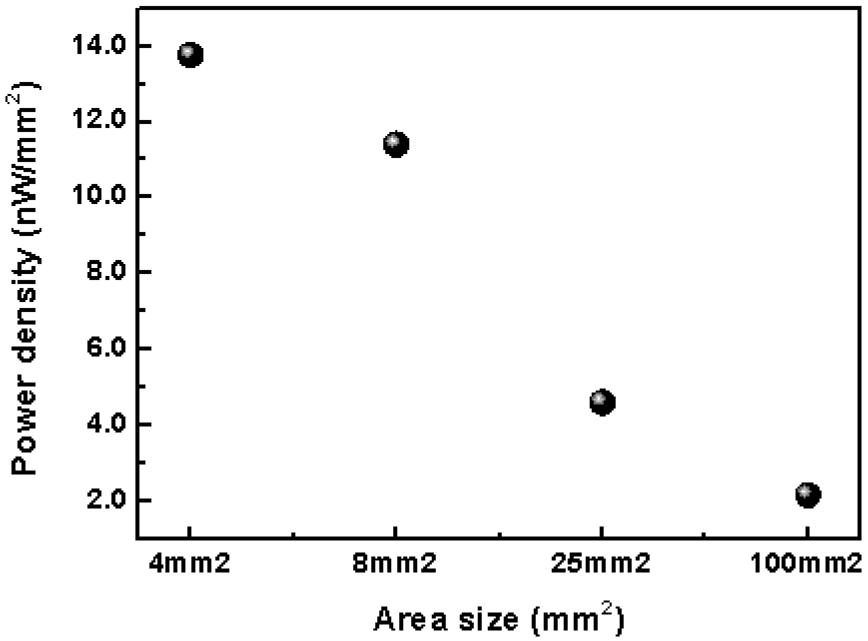
Figure 3.12 The values of electrical signals with controlled conditions. (a) The electrical signals are to the length of ZnO nanowires. (b) The larger the external pressure, the bigger the electrical signals.

3.4.4 Electrical signals with area grown ZnO nanowires

If ZnO nanowires have the same growth time, they can have an area effect. That means their power of per unit area can be different. As shown in Figure 3.13 (a), when the sample size was different and all ZnO nanowires on the sample was pressed, the larger the sample size, the bigger the current because current is affected by area size., if area is increased, current is also increased. However, voltage is not changed because the c-axes of the nanowires are aligned parallel to one another; the piezoelectric potentials created along each nanowire have the same tendency of distribution. Theoretically, the power should be increased according to the larger area. However, the actual result is different. When this experiment was carried out, the applied area that is the same size as the ZnO nanowires growth area is different, but the pressure is applied is the same. In case of large area, nanowires cannot be easily bent because of neighboring nanowires, but nanowires from the small area are almost bended at boundary. The magnitude of the piezopotential depends on the degree of deformation. In the linear eleasticity range, the piezopotential is proportional to the strain in the crystal. Therefore, small areas having nanowires from near the edge of sample generate larger piezopotential and power density is larger. The experiment to know effect of area size grown ZnO nanowires shows that the smaller the area, the higher the power density (see Figure 3.13 (b)). That means that if a touch sensor is made to be the size of a human cell, its efficiency is higher.



(a)

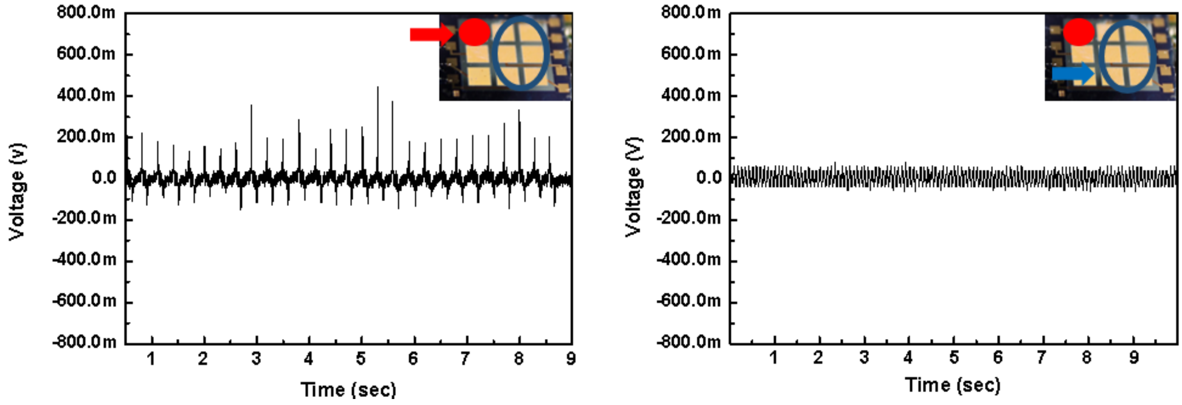


(b)

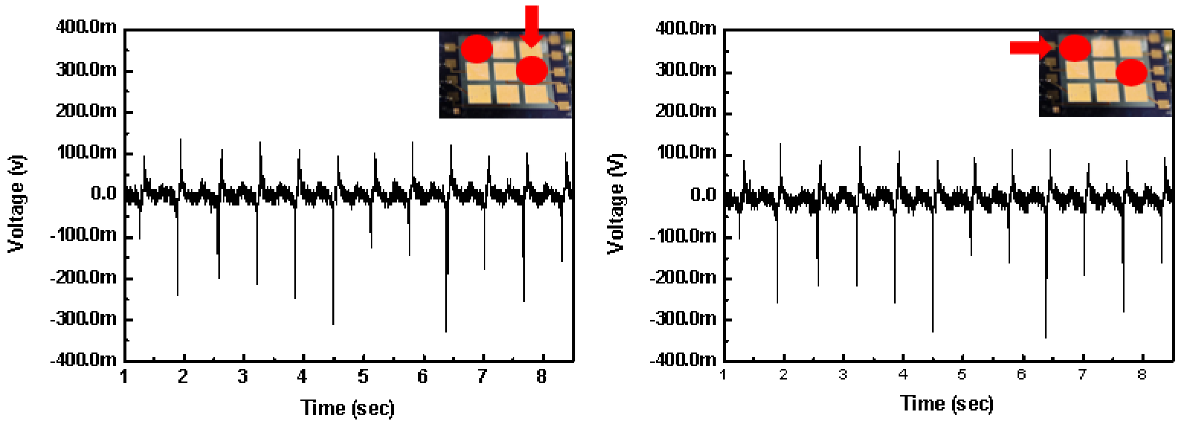
Figure 3.13 The values of electrical signals with area. (a) The larger the area size, current is increased, but voltage is not increased. (b) In occasion of the same applying pressure area, the power density per unit is increased when applied area is small.

3.5 Touch sensor ability

Prepared samples with 3 by 3 square patterns measuring 2mm by 2mm were used to know the probability as touch sensors. Each of the 3 by 3 square patterns has one's top and bottom electrodes to attach to wires. Therefore, all patterns as touch sensors can detect external pressure separately. Each wire attached to electrodes was connected to oscilloscopes, and the oscilloscopes showed the electrical signals when an external pressure was applied to the touch sensors. The pressed patterns generate the electrical signals depending on how much given external pressure. To know whether each pattern was operated or not, one of nine patterns was pressed. Then, the one pattern pressed generates an electrical signal, and the signal was checked by an oscilloscope, as shown in Figure 3.14 (a). The other patterns that were not pressed did not generated any electrical signals. Once again, the other one pattern in other position was pressed. It also generates electrical signals, and the others did not generate. When two patterns were pressed at the same time, they generate similar electrical signals as shown in Figure 3.14 (b). After this simple test, we measured the signals on the 9 patterns when giving external pressure by using two type of material with round tip and sharp tip over changing the pressing areas; whole area, a part of certain area, a boundary area between patterns. Each pattern generate its signals. To compare their electrical signal values, I classified the electrical signals in several colors. Figure 3.15(a) shows the first material having round and blunt tip. As shown Figure 3.15(b), the electrical signals with different external pressure condition and area which is pressed. Although the nine patterns have pressures at the same time, they get different pressures. And we can estimate external pressure to some extent by using image processing which transforms signals into colors. Furthermore, By analyzing the figure generating electronic signals and the size of them, we can guess the objects' size which made pressure on the patterns. In the Figure 3.16, we try again by using the other material with sharp tip.



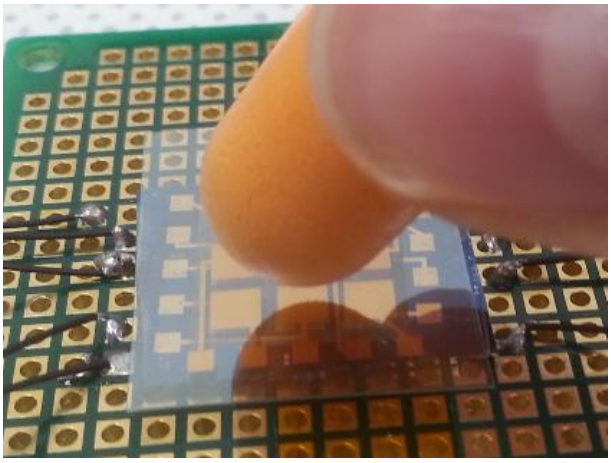
(a)



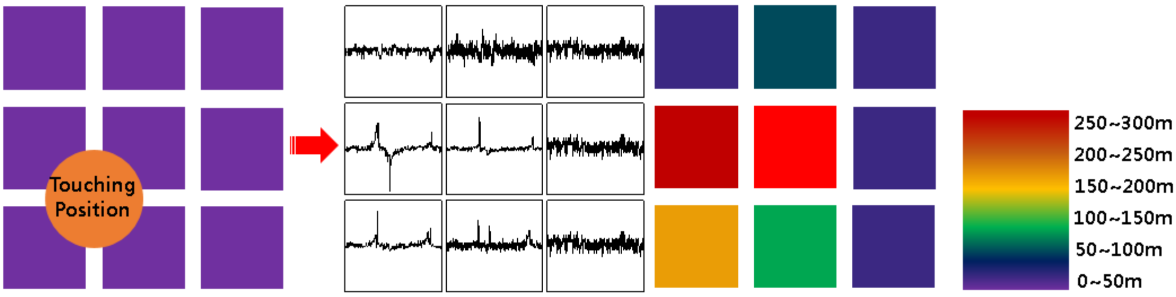
(b)

Figure 3.14 The values of electrical signals for touch sensor ability. The touched position is pointed by red arrow in the figure. (a) The one pattern was pressed, the others were not pressed. (b) Two patterns were pressed at the same time.

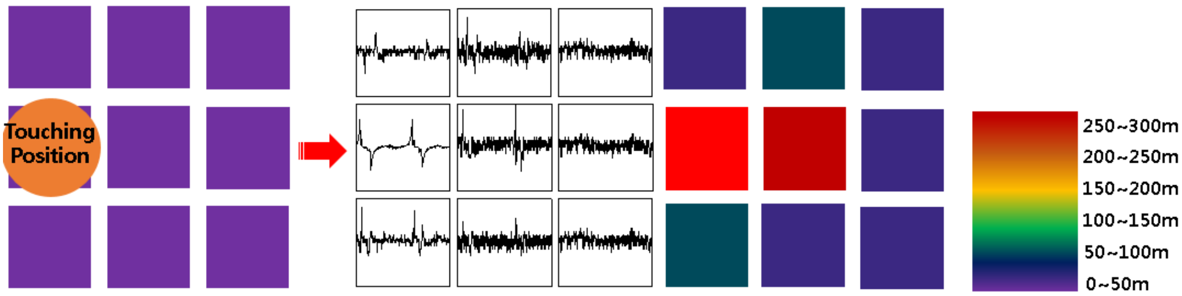
9 patterns also generated their electrical signals, and the electrical signals were transformed to image processing. The sharp material makes different signals compared with blunt material. In the case of using blunt material, a certain pattern what I want to press did not make that certain pattern signals due to the area of blunt material. The blunt tip of material causes some signals in the vicinity of the certain pattern. On the contrary, the sharp tip of material makes its own certain pattern signal because the sharp material did not affect other patterns in the vicinity of the certain pattern. We can check that difference between round material and shared material by using image processing



(a)

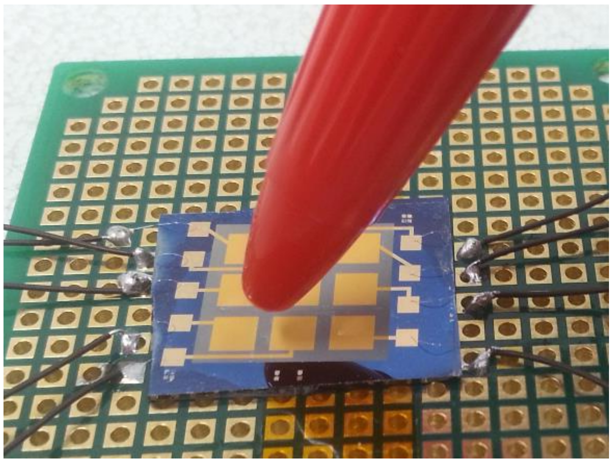


(b)

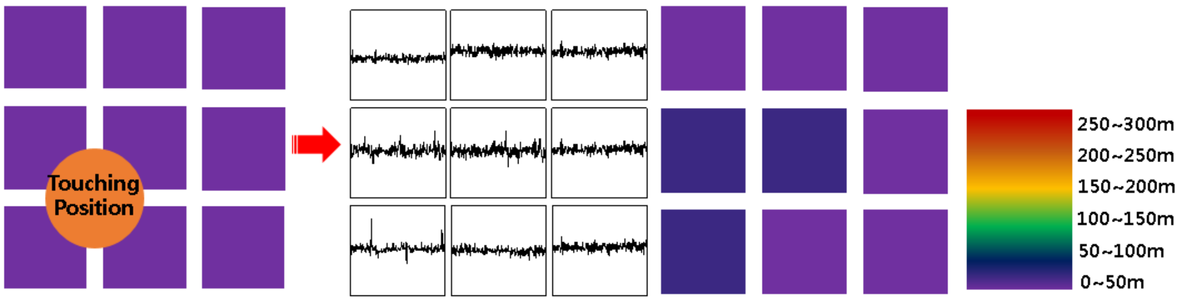


(c)

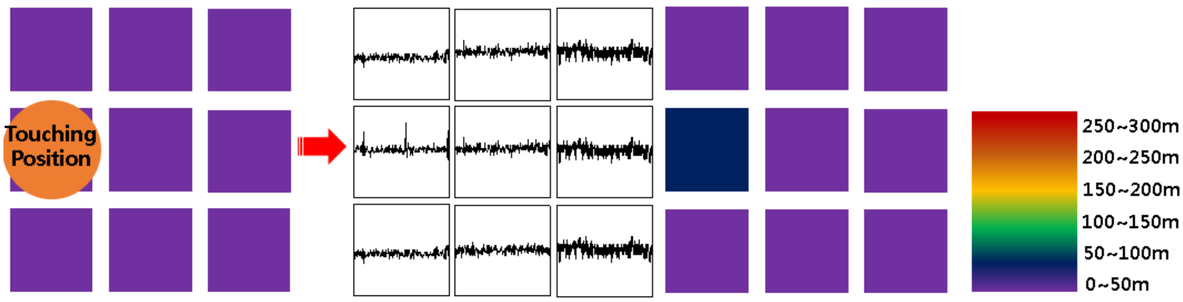
Figure 3.15 Test using blunt material. (a) The used material with blunt and round. It touched patterned sample over changing position. (b) The orange circle means touching position. When the pressure is applied to between four patterns, four patterns generated above 100mV electrical signals. (c) When a certain pattern position was touched, that one pattern position made the highest signals. Also, the blunt tip caused some signals in the vicinity of the certain pattern.



(a)



(b)



(c)

Figure 3.16 Test using sharp material. (a) The used material with sharp and narrow. It touched patterned sample over changing position. (b) When the pressure is applied to between four patterns, the affected three patterns generated weak signals. (c) When a certain pattern position was touched, that one pattern made a weak signal. The sharp material did not affect other pattern in the vicinity of a certain pattern.

. Such electronic signal difference would make it possible to distinguish what objects are. This experiments showed small pattern arrays on one substrate can be touch sensor arrays for electronic skin, and they can detect external pressure separately. Therefore, the probability of touch sensors for electronic skin was confirmed. In the future, if the touch sensor arrays that are similar in size to a human cell are developed, they will be electronic skin with high resolution.

IV. Conclusion

We have studied a new touch sensor concept which can generate some psychological feeling. To achieve the concept, we have presented several approaches for developing touch sensor arrays based on piezoelectric material, especially ZnO nanowires, promising semi-conductor material with a wide direct band gap, large exiton binding energy, high elasticity, and biocompatible among the piezoelectric materials. To make device structure with high performance efficiency, the piezoelectric effect was measured with the seed layer crystal orientation, the kind of metals, the length of wire, the change of pressure, and the cell size effect. Firstly, ZnO nanowires were grown by VLS method, but it usually requires high operation temperature. However, it is incompatible with plastic substrates for applications in flexible and wearable electronics. Otherwise, hydrothermal method can be grown ZnO wire at 80-100℃. Since many kinds of substrates including silicon, glass, and plastic can be employed, most of experiments in this research were focused to the hydrothermal method. To find optimized ZnO seed condition for growing vertical ZnO nanowires, several seed layer forming condition were controlled. Among several conditions, the seed layer formation at room temperature without any post annealing process shows an optimal vertical growth results confirmed by SEM images, XRD measurement and PL data. To operate touch sensor arrays individually, we need individual metal electrode for isolated touch sensors. The metal electrode should make Schottky barrier between semiconductor and metal. Some analyses such as work function of metals, X-ray diffraction and voltage measurement were carried out. When the combination of gold electrode having the highest work function and thin ZnO seed layer was formed, it showed the good crystallinity of ZnO nanowires and the piezoelectric power generation to about 600 nW. The property of length was confirmed with growth time every two hours for twenty four hours. The length of ZnO nanowires are proportional to the growth time from 0.25um to 3um. With increasing length of wire, the electrical signal was increased from about 80 mV to 150 mV. The current is also increased from 250 nA to 400 nA. Smaller cell structure produces higher piezoelectric power density due to the increase of effective edge area. Because the resolution of human fingers is very small, near 1mm, the small size effect of ZnO wire array cell gives other design merit for touch sensor application. Besides, the larger the external pressure, the higher the electrical signals. Based on previous experiments that presented optimized condition such as using gold layer, and growth time of twenty four hours, 3 by 3, 9 patterns were fabricated on one substrate to test ability of touch sensor. And then, they were measured the electrical signals when giving external pressure by using several material such as sharp tip or blunt tip. The generated electrical signals were different with materials. For instance, with the sharp tip, the electrical signals were generated within a piece of pattern, while, with blunt tip, they were shown with more extended patterns. We have converted the electrical signals into colors in order to do image processing system. Through the image processing system that classified the electrical signals, we could guess easily object's size which made pressure on the patterns. From these experiment results, we have completed basic research about testing possibility and ability of touch sensor. In the future, a touch sensor that have tiny pattern array as small as human cell dimension will be developed and it will have high resolution and can generate psychological feeling.

References

[1] Girão, Pedro Silva, Octavian Postolache, and José Miguel Dias Pereira. "Tactile sensors for robotic applications." *Measurement*, 2012.

[2] Xiaodan (Stella) Jia. "Tactile Sensing Using Elastomeric Sensors", *M.S. Thesis*, Massachusetts Institute of Technology, Massachusetts, USA, 2012, 111 pages.

[3] Mohsin Islam Tiwana. "Design of tactile sensors for robotic hand control and upper limb prostheses", *Ph.D. Thesis*, The University of New South Wales, New South Wales, Australia, 2014, 151 pages.

[4] Zhu, Guang, et al. "Functional electrical stimulation by nanogenerator with 58 V output voltage." *Nano letters* 12(6), 2012, pp.3086-3090.

[5] Kang, B. S., et al. "pH measurements with single ZnO nanorods integrated with a microchannel." *Applied Physics Letters* 86(11), 2005, pp.112105-112105.

[6] Zhou, Jun, et al. "Gigantic enhancement in response and reset time of ZnO UV nanosensor by utilizing Schottky contact and surface functionalization." *Applied Physics Letters* 94(19), 2009, pp.191103-191103.

[7] Xue, Xinyu, et al. "Surface free-carrier screening effect on the output of a ZnO nanowire nanogenerator and its potential as a self-powered active gas sensor." *Nanotechnology* 24(22), 2013, pp.25501.

[8] Lee, Sangmin, et al. "Super-Flexible Nanogenerator for Energy Harvesting from Gentle Wind and as an Active Deformation Sensor." *Advanced Functional Materials*, 2012

[9] Yu, Aifang, Peng Jiang, and Zhong Lin Wang. "Nanogenerator as self-powered vibration sensor." *Nano Energy* 1(3), 2012, pp. 418-423.

[10] Wang, Zhong Lin. "ZnO nanowire and nanobelt platform for nanotechnology." *Materials Science and Engineering: R: Reports* 64(3), 2009, pp.33-71.

[11] Wang, Zhong Lin, et al. "Progress in nanogenerators for portable electronics." *Materials Today* 15(12), 2012, pp.532-543.

[12] Lin, Long, et al. "High output nanogenerator based on assembly of GaN nanowires." *Nanotechnology* 22(47), 2011, pp.475401.

[13] http://www.embedded.com/design/mcus-processors-and-socs/4218309/Waking-up-a-capacitive-touch-sensing-device-with-an-MCU-peripheral

[14] https://spie.org/x38859.xml

[15] http://staff.aist.go.jp/maekawa.hitoshi/tactile/index_en.html

[16] http://en.wikipedia.org/wiki/File:Piezoelectric_sensor_electrical_model.svg

[17] Wang, Xudong. "Piezoelectric nanogenerators—harvesting ambient mechanical energy at the nanometer scale." *Nano Energy* 1(1), 2012, pp.13-24.

[18] V.A.Coleman and C.Jagadish. "Basic Properties and Applications of ZnO", The Australian National University, Canberra, ACT 0200, Australia, 2006, 20 pages.

[19] Diebold, Ulrike, Lynn Vogel Koplitz, and Olga Dulub. "Atomic-scale properties of low-index ZnO surfaces." *Applied surface science* 237(1), 2004, pp.336-342.

[20] Wang, Zhong Lin. "Nanopiezotronics." *Advanced Materials* 19(6), 2007, pp.889-892.

[21] Wang, Zhong Lin. "Piezotronic and piezophototronic effects." *The Journal of Physical Chemistry Letters* 1(9), 2010, pp.1388-1393.

[22] Yang, Ya, et al. "Pyroelectric Nanogenerators for Harvesting Thermoelectric Energy." *Nano letters* 12(6), 2012, pp.2833-2838.

[23] Zhiyong Fan and Jia G.Lu. "Zinc Oxide Nanostructures: Synthesis and Properties", *Ph.D. Thesis*, University of California, Irvine, CA 92697, USA, 2005.

[24] Yang, Peidong, et al. "Controlled growth of ZnO nanowires and their optical properties." *Advanced Functional Materials* 12(5), 2002, pp.323-331.

[25] Xia, Younan, et al. "One-dimensional nanostructures: synthesis, characterization, and applications." *Advanced materials* 15(5), 2003, pp.353-389.

[26] Wang, Xudong, et al. "Growth of uniformly aligned ZnO nanowire heterojunction arrays on GaN, AlN, and Al0. 5Ga0. 5N substrates." *Journal of the American Chemical Society* 127(21), 2005, pp.7920-7923.

[27] Hsu, Hsu-Cheng, et al. "Selective growth of ZnO nanorods on pre-coated ZnO buffer layer." *Journal of crystal growth* 261(4), 2004, pp.520-525.

[28] Guo, Min, et al. "Effects of preparing conditions on the electrodeposition of well-aligned ZnO nanorod arrays." *Electrochimica Acta* 53(14), 2008, pp.4633-4641.

[29] S.O.Kasap. *Principles of Electronic Materials and Devices*, McGraw-Hill, NewYork, 2006, 864 pages

[30] Xu, Sheng, et al. "Self-powered nanowire devices." *Nature Nanotechnology* 5(5), 2010, pp.366-373.

[31] Kumar, Brijesh, and Sang-Woo Kim. "Energy harvesting based on semiconducting piezoelectric ZnO nanostructures." *Nano Energy* 1(3), 2012, pp.342-355.

[32] Lin, Zong-Hong, et al. "BaTiO3 Nanotubes-Based Flexible and Transparent Nanogenerators." *The Journal of Physical Chemistry Letters* 3(23), 2012, pp.3599-3604.

[33] http://epswww.unm.edu/xrd/xrdbasics.pdf

요 약 문

전자 피부를 위한 ZnO nanowire를 이용한 터치 센서 개발

많은 연구 그룹들은 저항식, 정전식의 센서를 이용하여 모바일 기계나 안드로이드 로봇에 적용하기 위해서 터치 센서를 개발하고 있다. 하지만 이러한 터치센서들은 단순히 압력이나 압력의 분포만을 인지 할 뿐 인간이 느낄 수 있는 부드러움, 거칠기, 고통과 같은 정신감각적인 것들은 인식 하지 못 한다. 정신적인 감각 신호를 만들어 내기 위해서 우리는 압전 물질을 이용하여 터치 센서 어레이 개발을 시도하였다. 압전 물질을 이용한 터치 센서는 자가발전, 고분해능, 멀티 터치 등 다양한 부분에서 많은 이점을 가진다. 다양한 압전 물질 중에서도 ZnO 나노와이어를 이용한 고효율 디바이스 개발을 위해 다양한 종류의 ZnO seed 조건과 전극으로서의 메탈의 종류, Nanowire 의 길이, 외부에서 가해지는 힘 등을 변화시켜 나타나는 전기적 특성을 측정하였다. 실온에서 기판 위에 골드와 ZnO seed 를 증착시키고, 그 위에서 자란 ZnO Nanowire 는 다른 메탈에서 자란 것들 보다 수직성, 결정성이 좋은 것으로 나타났다. ZnO nanowire의 길이는 성장 시간에 비례하였고, 길이의 증가에 따라서 발생하는 전압은 80mV 에서 150mv 까지 증가하는 것을 확인 할 수 있었다. 전류 또한 길이가 길어질수록 250 nA 에서 400 nA 까지 증가하였다. ZnO nanowire 가 성장한 면적의 크기 또한 영향을 주는데, 그 면적이 작을수록 테두리 부분의 nanowire 효과로 더욱 큰 전기적 신호를 발생하는 것을 확인하였다. 인간의 손끝에서 느낄 수 있는 촉감 세포 단위는 $1mm^2$ 보다 작기 때문에, ZnO nanowire어레이가 작아 질수록 터치 센서로서의 기능적인 측면이 향상 될 것이다. 3x3 패턴 어레이를 만들어 뭉툭한 물건과 뾰족한 물건을 이용하여 9개의 패턴들의 특정 부분에 압력을 주고 발생하는 전기적 신호를 측정해 보았다. 물건의 모양이나 가한 힘의 정도에 따라 각각의 패턴들은 여러 신호를 발생시켰고, 영상처리를 통해 발생하는 신호의 크기를 여러 가지 색깔로 구분하였다. ZnO nanowire 를 성장시키기 위해 필요한 온도는 90℃ 이기 때문에 향후에는 유연하고 다양한 종류의 기판 위에 터치 센서가 개발 될 것이다. ZnO 나노 와이어를 이용한 터치 센서 개발의 기초 연구를 성공적으로 마쳤고, 이 논문의 실험 결과들은 앞으로 앞으로 자가발전이나 압전 디바이스 분야에 적용 될 수 있다.

핵심어: 나노 제너레이터, ZnO 나노와이어, 터치센서