Investigation of charge transport and photoexcitation effects in metal oxide nanonets

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NANYANG TECHNOLOGICAL UNIVERSITY

**INVESTIGATION OF CHARGE TRANSPORT
AND PHOTOEXCITATION EFFECTS IN
METAL OXIDE NANONETS**

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SCHOOL OF MATERIAL SCIENCE AND ENGINEERING

2012

INVESTIGATION OF CHARGE TRANSPORT AND PHOTOEXCITATION EFFECTS IN METAL OXIDE NANONETS

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Abstract

Tin oxide based, highly oriented metal oxide nanowire networks or ‘nanonets’ based devices are fabricated through photolithography free techniques. These nanonets studied at submillimeter scales in thin film transistors for macroelectronics & optoelectronics yielded good transparency and excellent electrical characteristics in vacuum. However, exposure of the SnO₂ nanonet transistors to the ambient atmospheres resulted in positive threshold voltage shifts due to electron trapping by oxygen at the nanowire surface, thus introducing barriers for both intra- and inter- nanowire electrons transportation. Device performance in air was improved by applying passivation layers such as polystyrene or SiO₂.

Electrical and photophysical studies confirmed that the top few atomic layers of the oxide nanostructure surface critically influenced device performance showing high photo-response and strong influence of ambient atmosphere, especially oxygen and water vapor. Doping of tin oxide nanowires with antimony allowed modulation of electrical properties, with 5% Sb yielding highly conducting nanonets whereas doping with 0.5% Sb resulted in excellent semiconducting properties as well as stability in ambient atmospheres. In addition to conventional electrical probe techniques, non-contact optical methods were also used to confirm the semiconducting behavior of the nanonets; whereas surface analysis indicated that antimony is likely to segregate to the surface thus providing a degree of passivation and thus environmental stability.

The significant role played by nanowire-nanowire junctions in the nanonet devices is investigated through a series of temperature-dependent charge transport studies and the existence of localized/trapped states at the junction sites is demonstrated as a function of changes in channel lengths and thus the number of nanojunctions present. These states are

detrimental to the semiconducting nature of the nanonets at low carrier densities caused by low conductivity or low wire density of the nanonets. However, semiconducting behavior will be greatly enhanced under the assistance of localized/trapped states at high nanowire densities or with higher carrier concentrations.

Photoexcitation effects are enhanced by coating the nanonet with absorbers such as poly 3 hexylthiophene, copper indium selenide, or metallorganic dyes. The immediate transfer of free electrons from the photo-sensitive material to the nanonet upon light illumination ensures a promising photo-detecting function and potential photovoltaic applications in either organic-inorganic hybrid, thin-film or DSC format. In addition, ambipolar devices could also be realized by combining p-type conjugated polymers and nanonet devices.

In summary, this study paves ways to an intensive understanding of the role of nanowire junctions in the nanonet-type electron transportation through precise control of the nanowire alignment, array density, the nanowire surface defects, the testing environment, and dopant concentration. Large-area uniformity testing demonstrates a pathway towards macro-electronic device integration. Together with photoexcitation study including the photovoltaic fabrication and characterization, these results suggest that SnO_2 nanonets that offer fault tolerance, flexibility, high transparency and stable electrical properties could form a very attractive material set with properties that can find applications in both electronics and photovoltaic energy harvesting.

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List of Acronyms and Symbols

1-D	One-dimensional
CNT	Carbon nanotubes
CVD	Chemical vapour deposition
CIGS	Copper indium gallium selenide
DSSC	Dye-sensitized Solar Cell
EDX	Energy-dispersive X-ray spectroscopy
FFT	Fast Fourier transformation
FE-SEM	Field emission scanning electron microscope
FET	Field-effect transistor
FTO	Fluorine doped tin oxide
HR-TEM	High-resolution TEM
LB	Langmuir-Blodgett
NIL	Nanoimprint lithography
Nanonets	Nanowire networks
Nanojunctions	Nanowire-nanowire junctions
NWs	Nanowires
PL	Photoluminescence
PV	Photovoltaic
PECVD	Plasma-enhanced CVD
PDMS	Polydimethylsiloxane
PS	Polystyrene
PLD	Pulsed laser deposition
SAED	Selected-area electron diffraction
THz-TDS	Terahertz time-domain spectroscopy
TFT	Thin-film transistor
TEM	Transmission electron microscope
TCO	Transparent conducting oxide layer
VLS	Vapour – Liquid – Solid
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
μ	Electron mobility

List of Acronyms and Symbols

σ	Conductivity
n_e	Sheet carrier density
C_g	Gate capacitance
V_{GS}	Applied gate voltage
V_{DS}	Applied drain voltage
V_{TH}	Threshold voltage
I_{DS}	Output current

Chapter 1

INTRODUCTION

1.1 Background & Motivation

The fabrication of high-performance devices (thin film transistors, diodes, solar cells) on cheap large area substrates such as plastic/metal foils is a target that traditional semiconductors such as amorphous silicon (a-Si) and polycrystalline silicon (poly Si) are ill-equipped to meet. Chemical-vapor deposition (CVD) process was generally adopted in the deposition process for Si film at temperature between 400-700°C, which is not suitable for plastic substrate. Besides, carrier mobility inside the amorphous Si is rather low ($\sim 1 \text{ cm}^2/\text{Vs}$)(1).

Organic thin film based devices have attracted attention recently due to their solution processability which enables low temperature processing compatible with plastic substrates and allows roll-to-roll printing techniques. However, they are ill-equipped to make high-performance flexible electronics due to the fundamental limits on material properties such as carrier mobility and material stability. Thin film transistors fabricated by these organic compounds possess only limited charge carrier mobility ($10^{-4} \text{ cm}^2/\text{Vs}$ to $1 \text{ cm}^2/\text{Vs}$ (max) including the organic-inorganic hybrid structure) which restricts these devices to low-frequency applications (2-4).

Besides the materials mentioned above, there has been growing interest in inorganic semiconducting nanostructures due to their potential applications on large-area, low-cost and flexible substrates. Synthetic inorganic nanostructures are highly flexible due to submicrometer diameters and with high-throughput and tailorable material properties such as shape, size,

atomic composition, and doping concentration (5-7). Hence they form a very attractive material set for large-scale printable electronics with elevated requirements on performance.

These semiconducting nanostructures are envisioned as building blocks in a wide variety of nanoscale electronic and photonic devices. Three material sets which are being widely explored include (i) carbon nanotubes (CNTs) and more recently graphene (7-9), (ii) silicon NWs (10-11) and (iii) metal oxide NWs (12-13).

To date, the research has focused on CNT nanotube networks which have been thoroughly studied and employed in field effect transistors, sensors as well as electronic circuitry. It is worth to note that carbon-based nanomaterials including carbon nanotubes (CNTs) and graphene have also demonstrated spectacularly high mobility(7, 14-17), especially the latter has shown carrier mobility up to $20,000 \text{ cm}^2/(\text{V}\cdot\text{s})$ at room temperature(18). However, a limiting problem for the CNT systems is the existence of metallic CNTs which conducts bulk of the current and dominates the charge transport properties. Although efforts to improve the ON/OFF ratios of these networks are being pursued through metallic nanotube separation as well as through ‘striping’ of the NW networks, it continues to remain a big challenge. On the other hand, band gap opening in graphene is rather challenging resulted in relatively low ON/OFF ratio (19-20). It shows a very weak optical response, and brings in noise when used as single layered electronic component, thus limiting the practical application.

Metal oxide NW networks are an attractive alternative due to ease of growth of NWs (grown through techniques not accessible to silicon NWs and carbon nanotubes) while still providing appealing electrical properties. Inorganic NWs have demonstrated excellent mechanical flexibility and high mobility (21-23), which provides us with a vast choice of materials for NW-

base high-performance flexible applications. Another key advantage is the possibility of doping to modulate both optical and electrical properties. Much of the work on metal oxide NWs have centered on ZnO where their applications in field effect transistors(24), sensors(25) and piezoelectric energy generators(26) have been demonstrated. On the other hand, 1D tin oxide (SnO_2) NWs with a large band gap (3.6 eV) also show significant potential for applications ranging from field-effect transistors(27-28), gas sensors(29-30), as well as solar cells(31). Oxygen vacancies and tin interstitials that have low formation energies create shallow donor levels lying below the conduction band and give rise to the high n-type conductivity of nonstoichiometric SnO_2 . Mobilities reported in both single crystal(32) SnO_2 ($\mu \approx 250 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) as well as nanostructures(33) ($\mu \approx 125 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are orders of magnitude higher than a-Si. Even though there are a number of factors that might affect the electrical and optical properties of SnO_2 NW, such as physical dimensions of the NW, amount and locations of Sn and O interstitials, as well as doping of foreign metal atoms, these have not been fully understood in literature.

In addition, the device structure design and characterization becomes very important since the application of NW in macroelectronics requires relatively large areas and depends on the optoelectronic properties of ensembles of these 1-D nanostructures. A new concept of NW-TFTs has recently been proposed and demonstrated using oriented semiconductor NW thin film semiconductor channels (34), which requires the transfer of NWs from the growth substrate. One of the most important aspects of the NW-TFT concept is the separation of material synthesis from device fabrication. Under this concept, the entire device fabrication process can be performed at room temperature except for the NW growth step, which is carried out separately. Thus devices on flexible substrate will become highly possible. Through the

dissociation process, the NW transistors will retain the carrier mobilities approaching those of single-crystal materials (high growth temperature required generally) and the low processing temperature in the same time, which will not only improve the existing technologies in macroelectronics significantly but also may enable an entirely new generation of flexible, wearable, and disposable electronics for computing, wireless communication or even energy harvesting and storage (35). An additional factor driving interest in this area is the relatively low lithographical constraints required for fabricating these devices and the cost benefits thus associated with them.

On the other hand, previous reports were predominantly based on single NW devices with relatively small channel lengths ($<10\ \mu\text{m}$) (27, 33, 36-37) and are not representative of the scales desirable in large-scale electronics. Besides, the electrical effect of NW-NW junction resulted from the scale-up has not been fully understood. The length, density and element doping of the NWs may all be significant parameters that affect the nano-junction property and hence the electrical behaviors. Since the metal oxide NWs are widely used as gas and photo sensors, the working environment will also play an important role in determining the performance of nanonet devices which needs to be clarified before application.

1.2 Objective

The overall objective of the project is to obtain extensive fundamental understanding of the charge transport properties in inorganic oxide nanowire networks so as to explore applicability of these as key materials in a wide variety of optoelectronic devices. This objective may be detailed as follows:

1. In depth understanding of the intrinsic and extrinsic parameters that affect the charge transport in tin oxide based NW network devices which include:
 - The role played by the oxygen/surface defects originated from the alteration of the growth conditions;
 - Carrier concentrations affected by the impurity dopants;
 - Quality and quantity of nanojunctions which regards to the nanowire alignment, nanonet density and channel length.
 - Effect of working atmospheres and passivation layers.
2. Systematic evaluation of the structure – property relationships in these polycrystalline nanowire networks. This includes the investigation of the carrier transfer mechanism, the activation energy and localized/trapped states inside the nanonets.
3. Identification of the important factors affecting the device applications in field effect transistors, photodetectors, and photovoltaic devices. Exploration of the effect of hybrid devices combining nanonet devices with photoabsorbers as well as p-channel materials.
4. The feasibility of large-scale applications of nanonet in macroelectronics which includes the device stability and uniformity.

In order to implement the work described above, the whole project is divided into the following detailed parts:

1. The relationship between the electrical performance and number of NW-NW junctions will be demonstrated by altering the length and density of the as-grown then transferred NWs and the FET channel length;

2. Intrinsic properties of as-grown NWs will be able to affect the electrical properties of nanonets. This can be achieved by altering the growth conditions like temperature, the background pressure and oxygen content in the carrier gas.
3. The device working environment will be also altered to study the surface states of oxide NWs. Strategies like surface passivation and impurity doping will be adopted in order to improve the electrical performance of SnO₂ devices to suit the real-life application. Device uniformity and stability and the function of NW-NW junctions in such cases will be discussed.
4. Temperature-controlled device characterization will also be introduced in order to calculate the activation energy, to examine the existence of localized/trapped states at the junctions sites and to confirm the polycrystalline nature of the nanonet;
5. The photoexcitation effect of hybrid system such as organic P3HT/nanonet, metalorganic dye/nanonet and inorganic CIS/nanonet will be demonstrated with the fabrication of photovoltaic devices. The effect of physical properties of NW on the performance of DSCs will also be discussed.

1.3 Scope of the thesis

In **Chapter 2**, intrinsic properties of tin oxide in the format of both bulk and thin film are firstly touched, following by brief review on the diverse techniques for NW growth and NW network assembly. Doping of oxide NWs to improve the electrical properties is also presented. In addition, the electrical properties of metal oxide NWs esp. tin oxide NWs are reviewed and discussed in the last part.

Chapter 3 introduces the experimental procedure for growth of SnO₂ NWs by chemical vapor deposition and the fabrication of nanonet field-effect transistor. On top of these, the method for element doping and surface passivation will be mentioned as well. The characterization tools for as-grown NWs and nanonet based devices are also briefed.

Chapter 4 shows the results of as-grown NWs and the performance of nanonet-based devices which includes the following sub-sections:

- The channel length and NW density dependence of the device performance is highlighted following by a proposed model of electron transfer inside the nanonets. The performance of NWs with surface passivation is reported in the same section combined together with the device stability and uniformity testing for large-scale application;
- The effect of intrinsic and environment-related properties of tin oxide NWs on the performance of nanonet device is discussed here. The electrical properties of NWs with controlled amount of impurity doping are also listed. The localized/trapped states at inter-NW junctions will be revealed in this section via low-temperature characterization and detailed discussion;
- Hybrid system is fabricated and the interaction between NWs/polymer or CIS or dye are discussed. Application of nanonet as charge collectors, nanonet based devices such as DSCs are also fabricated and characterized.

In **Chapter 5**, brings the overall summary and conclusion. Along with the conclusion, future prospects addressing the large-scale device fabrication on flexible substrates through all-printed techniques and circuit integration hence industrial application are proposed in **Chapter 6**.

1.4 Scientific highlights

- 1) Highly oriented and uniform nanonets with area up to 1 x 1 cm² were prepared by contact printing using self-built apparatus, yielding high charge carrier mobility; achieving a simple way to passivate the SnO₂ nanonet devices. These methods can be transfer to other nanowires and nanobelts
- 2) Identifying key transport mechanisms and device physics pertinent to NW networks devices and investigating in particular role of oxygen and surface defects stemming from growth conditions and environment, including passivated devices.
- 3) Systematic studies of the density of the NW network and associated integration strategies, and resulting device performance.
- 4) Drawing a density of states picture and inter-wire transport, and in particular, looking at the activation energy and effects of localized/trapped states inside the nanonets.
- 5) Exploring new hybrid device structures based on inorganic-organic systems for photodetection as well as p-channel FETs. The new SnO₂ nanonets were used to fabricate dye sensitized solar cells with dye N719, as possible replacement of titania, thus opening a route for improved solar cells through proper control of nanowires properties.

Four 1st-authored journal papers (including submissions) and four equally-contributing 1st-author papers are published based on the findings as well as one international patent (refer to publication list attached).

Chapter 2

LITERATURE REVIEW

2.1 Introduction to Metal Oxide / Tin Oxide

A material is usually selected for a specific application based on its intrinsic properties, which include both bulk and surface (thin film) properties. The intrinsic properties of SnO_2 (including impurity doped SnO_2) leads into three major applications: (i) as transparent conducting oxide layer (TCO); (ii) as solid state gas sensing material and (iii) as an oxidation catalyst. While bulk properties are responsible for making SnO_2 a transparent conducting layer, the latter two applications are mainly relying on the surface reactions. Thus, surface properties are of direct relevance.

2.1.1 Bulk properties of SnO_2

Tin oxide is a typical n-type semiconducting metal oxide material, showing transparency with high chemical and mechanical stability. Rutile or cassiterite is the only one stable phase known that has a tetragonal arrangement of the atoms. This crystalline structure consists of metal atoms in octahedral coordination and oxygen in planar three-coordination having a lattice parameters of $a=4.737 \text{ \AA}$ ($a=b$ in tetragonal structure) and $c=3.186 \text{ \AA}$ (38).

In SnO_2 , chemical bonding is determined by the linear combination of oxygen 2s and 2p orbitals with tin 5s and 5p. It has a direct band gap of 3.6 eV (39). The features of the electronic structure of SnO_2 are determined by the band structure calculated as seen in Figure 2.1. It shows the conduction band for tin oxide is a single band of s-type character that is strongly dispersed with a minimum at the Γ -point of the brillouin zone, resulting in a light effective mass

($0.3 m_0$) of the conducting electrons (compared with the heavy holes in the same material) and thereby giving rise to an uniform distribution of the electron charge density hence relatively low scattering (40). These combined features contribute to the high mobility of the electron charge carriers in the material. It is reported to have resistivity of $10^{-4} - 10^6 \Omega \cdot \text{cm}$ (impurity doped/undoped), which is considerably lower than most semiconductors. Undoped SnO_2 can have a notable high carrier density of up to 10^{20} cm^{-3} which is comparable to that of semimetals ($10^{17} - 10^{20} \text{ cm}^{-3}$)(41).

Figure 2.1 Band structure calculations for SnO_2 (reproduced from (40) with permission)

Since perfectly stoichiometric tin oxide samples are highly resistive(42), electrical conduction in undoped SnO_2 is suspected to correlate with nonstoichiometry and with oxygen-related intrinsic defects due to the fact that the conductivity of tin oxide films changes exponentially with controlled variation of oxygen partial pressure (the power-law dependence $\sigma_{\text{el}} \sim p_{\text{O}_2}^{-1/6}$ of the electric conductivity on the oxygen partial pressure, which is characteristic for doubly positive oxygen vacancies (V_{O}^{2+}) (43)).

The coexistence of conductivity and transparency in SnO_2

Being wide band gap material, SnO_2 is a transparent conductor with optical transparency up to 97% in the visible range ($400 < \lambda < 700$ nm, for films thickness of 0.1-1 mm) (41). Another remarkable property of SnO_2 and other TCOs is that they are highly reflective for infrared (IR) in spite of the transparency in visible light, which makes SnO_2 one of dominant candidates as energy conserving materials (such as “smart window”).

The presence of transparent conductivity in these materials is due to the existence of shallow donor levels near the conduction band formed by a large concentration of oxygen vacancies (44-45). Due to single and double ionization of oxygen vacancies, these levels have energies of 0.03-0.034 eV and 0.14-0.15 eV below the conduction band minimum (CBM) (46-47). In a separate study, Kiliç and Zunger (44) carried out first-principles calculations (based on density functional theory in the local-density approximation (DFT-LDA)) of formation energies and electrical (donor, acceptor) levels for various intrinsic defects which showed that defect levels for oxygen vacancies lies 0.114 eV below the CBM and that can be easily thermally ionized.

2.1.2 The surface properties (gas sensing).

There are number of metal oxides that are suitable for detecting combustible, reducing, or oxidizing gases. Usually changes in the electrical conductance in response to environmental gases are checked even though exact fundamental mechanisms that cause the changed electrical response are still under investigations..

It is commonly believed (48) that when a molecule adsorbs on the oxide surface, electrons can be transferred from/to this molecule depends on the position of the lowest unoccupied molecular orbitals (LUMO) of the adsorbate complex and the Fermi level of the solid. Thus a net charge accumulation may be induced by the molecular adsorption at the surface which

results in an electric field. This electro-static field causes a bending of the energy bands in the solid. As illustrated in Figure 2.2, negative surface charges bend the bands upward, resulting in an electron depletion zone. To compensate for the negative surface charge, these depleting electrons cause a positive space charge region which alters the sheet conductivity σ accordingly. This change in conductivity is captured and used as the relevant signal in gas sensing devices.

Figure 2.2 Schematic illustration of band bending in the near surface region of an n-type metal-oxide semiconductor induced by negative surface charges. (reproduced from (38))

As surface sensing material, the dispersing conduction band of SnO_2 with its minimum at the Γ -point and the high mobility of the charge carriers ensures that a tiny alteration in charge carrier concentration results in a strong change in electrical conductance of the material (48), thus triggering a gas response signal. The sensing properties are normally performed in the format of thin films, either densely packed or porous.

In a short, it is obvious that for metal oxide semiconductors / tin oxide material, both the bulk and surface properties are playing very important roles during material application. The abundant oxygen vacancies provide the free carriers for the TCO application while the surface response to absorbents result in the gas sensing properties. However, the material used here are either epitaxial or polycrystalline (porous) thin films where they provide either relatively small

surface area or poor transportability due to multi-grains (back to back Schottky barriers at the grain boundaries). In contrast, metal oxide NW networks provide large surface to volume area with high electron transportability and superior stability due to the single crystalline nature (can be obtained by high temperature process), and will be introduced in details in the following section.

2.2 One dimensional metal oxide semiconductors

A NW is a nanostructure with its diameter in the order of a nanometer. Typical NWs exhibit aspect ratios (length-to-width ratio) of 1000 or more which is why they are often referred to as one-dimensional (1-D) materials. At these scale, quantum effects may dominate and are sometimes more important than the bulk properties. The fundamental difference is electrons are quantum confined laterally in NWs and thus occupy energy levels that different from the traditional continuum of energy levels or bands found in bulk materials, providing the NWs with unique properties not seen in bulk. Numerous types of NWs exist, ranging from metallic (e.g., Ni, Pt, Au), semiconducting (e.g., Si, GaN, ZnO, etc.), to insulating (e.g., SiO₂, TiO₂).

Two material sets of semiconducting NWs which are being widely explored include (i) silicon NWs and (ii) metal oxide NWs. Silicon NWs as the channel material are of particular interest because they could allow the combination of 1-D transport and self-assembled processing with the well-known Si technology. Metal oxide NW are an attractive alternative to Si NWs due to ease of growth of NWs (grown through techniques not accessible to silicon NWs) while still providing attractive electrical properties. Other advantages of these NW include access to a large range of bandgaps (energy gap of CuO=1.2eV; of ZnO=3.4eV) which enables their utilization in

photovoltaics as well as for transparent conducting electrodes, while impurity doping allows the modulation of both optical and electrical properties.

A variety of methods have been used to grow oxide NWs which mainly can be categorized into two big branches: top down and bottom up.

2.2.1 The synthesis of nanowires-top down approach

The **top down approach** is based on standard micro-fabrication methods using sculpting or etching to carving structures from a large piece of material in a subtractive fashion, including the diminution of the lateral dimensions of the films to nanometer size(49). Top down process such as optical and electron beam lithography consistently demonstrate their superiority in the nanometer control of device definition and placement (Figure 2.3)(50-51). Mature technology from the semiconductor industry is used in this approach which enables precise location control, large-scale fabrication and the capability to work on planar surfaces. Drawbacks are the elevated costs and longer preparation times which do not fulfill the industrial cost-effective requirements. Besides, the nanostructures produced using these approaches are mostly not single crystalline (strongly depends on the substrate used).

Figure 2.3 (a) High resolution features produced by EBL: nested lines at a pitch of 14 nm (43); (b) SEM image of an array of Si NWs with 50 nm diameter (through etching). Sputtered Al_2O_3 mask patterned by EBL was used as the etching mask. (51)

2.2.2 The synthesis of nanowires-bottom up approach

Another major category is **bottom up approach** including vapor phase transport, chemical vapor deposition, electrochemical deposition and solution phase approaches. The most remarkable advantages are the high purity, crystallinity and small diameters of the nanostructure produced and the ease of equipment setup, besides, impurity dopings can also be easily achieved in this way. While each specific method used may result in the dissimilar material crystal structure as well as other physical properties, the vapor phase methods generally producing NWs of the highest quality in terms of crystallinity. On the other hand, the need to produce large quantities of NWs cost-effectively as well as the high temperatures employed in vapor phase growth has given rise to the exploration of a wide variety of solution based techniques.

Vapor-Liquid-Solid (VLS) growth

Metal nanocluster assisted growth of NWs from gaseous species have attracted tremendous attention owing to the feasibility in creating defect-free 1-D structures of a variety of materials including oxides NWs (29, 52-54). Foreign metal catalyst mediated 1-D growth was originally developed in the context of Si whisker growth by Wagner and Ellis (55-56). The vapor-liquid-solid (VLS) mechanism of metal catalyst assisted growth is named for the different phases through which the NW material traverses during the growth process. The growth essentially involves three steps as illustrated in Figure 2.4 & Figure 2.5(57): 1) Formation of catalyst metal nanodroplets via heating; 2) Adsorption and dissolution of gaseous precursors in catalyst nanodroplets; and 3) Precipitation of the NW material from the supersaturated liquid.

Figure 2.4 Schematic illustration of vapor-liquid-solid NW growth mechanism including three stages, namely: (I) alloying, (II) nucleation, and (III) axial growth.

Figure 2.5 In situ TEM images recorded during the process of NW growth. Reproduced from (57)

VLS mechanism is generally applicable to diverse class of materials and it allows the growth of NWs with precise composition, crystal structure and microstructure(53). The catalyst nanoclusters promote the unidirectional growth by catalyzing the dissociation of precursor reactants and reducing the energy barrier that is required for the incorporation of new materials into the growing NW. Furthermore, the use of metal catalyst largely reduces the activation energy required for the growth of NWs as compared to non-catalytic growth. The catalyst remains at the free end of the NW and its presence is indicative of the VLS mechanism as shown in Figure 2.6(c). As suggested by Figure 2.5 and Figure 2.6(c), the diameter of the NWs was mainly controlled by the size of the catalyst clusters which remain almost constant during the NW growth. Thus it is feasible to tune the NW diameters simply by applying metal catalysts of appropriate size(58).

VLS growth route was found to be efficient in the synthesis of wide varieties of metal oxide NWs (59-62). Various techniques including chemical vapor deposition (CVD), metalorganic chemical vapor deposition (MOCVD), and pulsed laser deposition (PLD) were used to grow NW through VLS route. The simplest and widely adopted technique for metal oxides NW growth is CVD based on tube furnace. To produce the reactant vapors required, techniques including thermal evaporation(63) and carbothermal reduction(59, 64) of respective metal/metal oxides powder were routinely employed. The vapors produced were transported towards the growth substrates (covered with catalyst nanoclusters) by carrier gases (typically argon). High aspect ratio 1D nanostructures of binary metal oxides such as ZnO, SnO₂, Ga₂O₃, In₂O₃, Al₂O₃, MgO and V₂O₅ were synthesized through this way (60-62, 65-68). Figure 2.6 shows the growth and characterizations of MgO NWs on MgO (100) substrates. The NWs grow epitaxially on the substrate with the long axis along the [100] direction(66). In addition, the tuning of electrical and optical properties of NWs is accessible with ease through impurity doping in VLS growth mode(67-68). The feasibility of VLS route to create hybrid oxide NWs including core-shell and branched structures has also been demonstrated (67, 69)

Figure 2.6 (a) SEM image of MgO NWs grew on MgO substrates via VLS route. (b) XRD spectrum of the as-obtained NWs. (c) TEM image and SEAD pattern showing the [100] preferential growth direction. (reproduced from (66))

An important issue associated with the VLS growth of oxides NWs is the incorporation of catalyst metal into the NW. Such unintentional doping may deteriorate the NW electronic functionality and may be detrimental to its application in photovoltaics and nanoelectronics. In addition, despite the large effort that has been devoted to the catalyst assisted growth of metal oxide NWs, the VLS mechanism remains controversial(70-71). There is much debate over the physical state of catalyst particle during VLS growth. ZnO NWs, for example, grow via VLS route over a broad range of temperatures. A vapor-solid-solid (VSS) mechanism instead of VLS mechanism was proposed for the growth of ZnO using gold catalyst at low temperatures (72).

Besides, there are always issues with the high process temperature generally required and low yield which retard it from industrial mass production.

Solution based techniques

An alternate route towards sustainable low-cost fabrication is solution-based techniques, which have advantages such as low temperature process, high yield and easy fabrication. NWs are grown at lower temperature ($<200^{\circ}\text{C}$) where the growth is driven by chemical decomposition of precursors in the solution rather than physical decomposition (In VLS techniques). Through these techniques, NWs with excellent control over the shape and composition have been demonstrated (73-76). They provide a promising approach for mass production of a variety of NWs, including metal oxides. One of the most common and well explored techniques for growing NWs from solution is hydrothermal synthesis where the growth starts with the immersion of a substrate in a heated liquid solution, as shown in Figure 2.7(77). Hydrothermal growth was first introduced to grow single crystals of semiconductors and several different metal oxide NW have since been grown by the same method, such as In_2O_3 , Ga_2O_3 , and MnO_2 , as well as more complex perovskite structures.

Figure 2.7 Schematic view of the hydrothermal growth of NW: (a) The precursors are heated and (b) reactive (hydroxyl) ions react with metal ions to form metal oxide; (c) ZnO NW as grown. (77)

Hydrothermal techniques allow assembly of nanocrystals with other functional materials to form hybrid nanostructures for applications in nanoelectronics(78) and biological systems(79). Apart from hydrothermal growth, other important solution based techniques like anodization(80) is also able to generate high quality nanostructures with controlled arrangement. The main drawback of solution grown NWs is that they show relatively lower levels of crystallinity, compared to VLS and similar techniques involving higher temperatures.

2.3 Doping of metal oxide materials

Since the semiconducting behavior and the number of charge carriers in metal oxides are mainly dependent on oxygen defects which are impractical to control, doping of these oxides have been pursued in order to better manipulate their electrical properties. Theoretically, a donor impurity in the metal oxide material such as antimony or fluorine in tin oxide and aluminum in zinc oxide, increases free electron concentration hence the n-type conductivity. On the other hand, a lower valence cation as acceptor impurity such as indium or aluminum in tin oxide and zinc in indium oxide, produces a hole hence increases the hole concentration which results in the p-type conductivity. Doping is especially important for the fabrication of air-stable devices, since the increased charge carrier density leads to a shorter Debye length, making the charge transport in NWs more stable regardless adsorbents on the NW surface. It is worth noting that p-type doping of these naturally n-type oxides has been proved to be difficult to achieve due to self-compensating doping mechanisms by the native defects. Phosphorus(81) and Sodium(82) doping in ZnO NWs to induce p-type behavior are recent successes with no evidence of instability has been reported.

2.3.1 N-type doping

Sb is a common n-type dopant in SnO_2 . Careful control of the doping density of Sb in SnO_2 produced NWs with high charge carrier mobility ($550 \text{ cm}^2/\text{V.s}$) at low doping concentrations while high concentrations lead to the formation of a conductor with a resistivity of $5.8 \times 10^{-4} \text{ Ohm}\cdot\text{cm}$ (83). Sb dopant which is mostly in the valency of 5+ will substitute Sn in the rutile structure and therefore contribute one free electron. In this case, the band structure will be modified upon the impurity doping and band structure calculations for Sb doped SnO_2 (Figure 2.8(b)) suggests that the formation of a Sb 5s like band in the SnO_2 band gap with a free electron-like character at the Γ - point, which results in the significant increase of the free carriers hence the conductivity(40).

Figure 2.8 Band structure calculations for (a) SnO_2 , (b) Sb doped SnO_2 . (reuse from (40) with permission)

2.3.2 P-type doping

To fabricate optoelectronic devices with oxide-based p-n junction, it is essential to obtain high quality p-type material. Through calculations, researchers from UCSB(84) found that p-type doping in SnO_2 is theoretically easier to achieve than in other oxides such as ZnO . They claimed that substitution of group-IIIA atoms (In, Ga, and Al) on the Sn site generates shallow acceptors

that exhibit good solubility and a low degree of self-compensation. Several groups have reported the successful p-type doping of SnO₂ films employing dopants like Al, Li or In by spray pyrolysis (85-87). However, the reported p-type doping cases done by spray pyrolysis are all dependent on dopant/host ratios with a narrow opening (such as Al-doped SnO₂ films, the conversion of majority carriers from electrons to holes only when the dopant concentration is close to 8 at% in the film. For Indium doped tin oxide thin film, indium plays as acceptor only with In / Sn ratio of 0.1 and 0.2; further increase of the In /Sn ratio will revert the film to n-type due to the appearance of indium oxide phase). Besides, Hall-effect measurement was adopted in order to characterize the acceptors without any real field-effect device fabrication.

Although it is anticipated that doping with group V acceptors would be difficult to achieve since all the group V elements have significantly lower electron negativity than O (84), Pan, S.S., et al. has managed to obtain atomic N-doped SnO₂ films via reactive sputtering at high nitrogen partial pressure which exhibit p-type conduction (88). However, compared with the electron concentrations in pristine n-type SnO₂ films (10^{18} – 10^{20} cm⁻³), the hole concentrations in atomic N-doped p-type SnO₂ films (10^{11} – 10^{14} cm⁻³) is too low to realize the SnO₂-based p-n junctions. To enhance the hole concentration and mobility, the authors proposed epitaxial growth of single crystalline films doped with nitric oxides (NO, N₂O) or NH₃ as N source, and maybe Al (or In, Ga)–N dual acceptor co-doping, yet the results have not been reported.

2.4 Nanowire Network Assembly

Bottom up approach via VLS technique to obtain metal oxide NWs with desired composition has been widely adopted due to the simple setup along with the better quality, and it is also used in the current study. The main disadvantage of this bottom up approach is the fact that the as

grown nanostructures are normally with random orientations unless epitaxial substrate is adopted, which make the integration of these nanostructures on planar substrates difficult for the purpose of either exploration or large area application. This is the reason why a specific procedure is required to assemble the NWs onto specific substrate to assure their reliable integration into functional devices, which will be introduced in the following chapter. Besides, the NWs are normally fabricated under high temperature in VLS processes, which make the following procedure more necessary if plastic/flexible substrate is required.

Figure 2.9 (a) Flow directed assembly of NWs(89); (b) Process flow for creating Langmuir-Blodgett assemblies(90) (c) Large scale "surface programmed" assembly of V_2O_5 NWs(91). (d) Schematic of bubble-blown NW assembly method(92).

The importance of alignment: it is essential to assemble NWs with controlled orientation and interspacing over large areas in order to fabricate high-performance devices and complex logic circuits. NWs with random alignment in this application can cause the degradation and nonuniformity of the large-scale device performance.

In order to control the location and alignment of these nanostructures on the desired substrate, many strategies with precise control and repeatability have been pursued. These include flow alignment strategies(93), Langmuir-Blodgett assemblies(90, 94-95), surface programmed assemblies(91), as well as bubble-blown NW assembly(92), as shown in Figure 2.9. These strategies all involve the suspension of the NWs in an appropriate solvent by ultrasonication the growth substrate before integrating them on to the substrate of interest.

The **flow-assisted NW alignment(93)** process pioneered by Lieber and co-workers utilized the shear force of fluidic motion and incorporate microfluidic channels on the desired substrate (with molecular patterns) to enable the directional flow of the suspension resulting in assembly of NWs according to the flow direction (Figure 2.9a). The micro-channel is commonly formed on Polydimethylsiloxane (PDMS) and can extend to almost millimeters. This flow-directed technology can also be used to align the NWs into crossed or even more complex structures, which enables device array construction. Although circuitry fabrication(11, 96) has been demonstrated on such assembled NWs, including on plastic substrates(97-98), the limited density of the NWs in such networks makes this technique unattractive. The area of NW alignment is also restricted by the size of the fluidic channels with larger channel resulted in non-uniform shear force hence NW networks.

The **Langmuir-Blodgett (LB)** approach consists of floating a NW-surfactant phase on the surface of liquid (water or organic solvents) as shown in Figure 2.9b. The application of a compressive force via a barrier to the floating NW monolayer results in the densification of the aligned NWs so as to minimize the surface energy of the liquid. The aligned NWs can then be transferred onto the appropriate substrate (95, 99-100). A related assembly technique called Langmuir-Schaefer technique has also been used to fabricate FETs (101). Many researchers have made use of this technique to assemble various NWs into large scale devices. It has also been proved to be an attractive way to fabricate devices with complex structures. However, the slow process and strict control condition retard the mass application. Besides, NWs have to be functionalized in the beginning of the process which may alter the surface properties of metal oxide NWs.

Surface programmed assembly involves forming patterns of Self-Assembled-Monolayers (SAMs) on the surface of the receiver substrate through conventional techniques(91). These patterns induce a difference in the surface properties (charged vs. uncharged, hydrophilic vs. hydrophobic, functionalized vs. unfunctionalized) which would allow the NWs from the solution to be preferentially adsorbed on to one of the regions (Figure 2.9c). SAM patterns can be created through locally attaching the molecules on the substrate surface (through microcontact printing(102-103) , dip-pen lithography(104-105)) or by selectively removing molecules from a layer through UV light illumination. Surface programmed self assembly has been employed in assembling V_2O_5 NWs(106) by patterning SAM molecules to create positively charged and neutral surface regions. V_2O_5 NWs which are negatively charged in aqueous

solutions are attracted to the positively charged regions of the substrate, assembling to form ordered structures.

Bubble blown NW assembly (92) makes use of the shear force generated by the expansion of a bubble-blown film with the process as shown in Figure 2.9d. Basically, a homogeneous NW suspension in specific polymer was first prepared. The suspension was then dropped onto a circular dye followed by blowing the dye into a bubble. 85% alignment of the NW can be achieved during this process under controlled expansion rate and blowing pressure. The transfer process was completed by bringing the desired substrate in contact with the NW bubble. However, it is obvious from experimental data that the density of NW network obtained was rather low which is inevitable since the expansion of the bubble separate the NWs apart while aligning them.

Despite significant progress made in the methods described above, the techniques are not well adapted for the fabrication of high density networks at larger scales. An alternative which is gaining attention is direct contact which has demonstrated easy scalability of network formation at high throughputs.

Figure 2.10 Schematics of NW contact printing. Reproduced from reference (107)

Contact printing approach involves the direct transfer of NWs from the growth substrate to the receiver substrate through shear force(107). In this process, the growth substrate with vertically grown NWs is brought into contact with the receiver substrate and gently slid along a particular direction, as shown in Figure 2.10. While shear force is utilized to align the NWs effectively, van der Waal's force of attraction and other chemical binding interactions between the substrate and the NWs allow the NWs to anchor to the receiver substrate. This allows the formation of well aligned NW networks of high crystallinity even on unconventional substrates such as plastic and glass. Javey and co-workers have extensively explored this technique and have demonstrated wafer scale assembly of Si, Ge and CdSe NW arrays which allowed them to be integrated into transistors and sensors via a lubricant-mediated mechanical rubbing transfer(108-110). Besides, this process can also be used in combination with lithography patterning which allows NW transfer onto a substrate selectively.

Figure 2.11 Schematic representation illustrating the process of NW assembly with the respective optical images showing the alignment process of Si NWs on PDMS substrate before (left) and after (right) the strain was released. Reproduced from reference(111).

The alignment of inorganic NWs can be assisted by a strain-release assembly method on stretchable substrates(111). In this case, NWs are contact-printed to a stretched PDMS substrate first followed by releasing of the strain (Figure 2.11). The gap between NWs will close up during the strain releasing process which results in the parallel aligned NW networks along the direction perpendicular to stretching with enhanced NW density. The nanonet can be transferred afterward to desired substrate for device fabrication. Obviously, substrate which can provide large-strain elasticity is the essential factor here during the transfer.

Roll-to-roll transfer printing of NWs based on contact printing process was also realized by the same group(112). The essential part is the NWs have been to grown on a cylindrical substrate. The rolling process is with speeds up to 20 mm min^{-1} . Even though the printing speed is from

industrial manufacturing requirement, these experiments proved the potential of this technique for printable NW electronics.

In a word, direct-contact printing is a very promising methodology even though several issues still need to be addressed. One of the unfortunate consequences of contact printing is the reduction of NW length due to the shear stress involved. Javey's group claimed that employing lubricant during transfer can improve the alignment and length of the NW transferred. However, mild O_2 – plasma (30W, 30s) was applied to remove the lubricant which is a big concern if the transferred material is metal oxide NW. Besides, the need for vertically aligned as-grown NWs and the affinity of oxide semiconductor surfaces toward adsorption of ambient gases (e.g., oxygen, water vapor) are challenges that warrant attention.

2.5 Electrical properties of metal oxide nanowires

The semiconducting nature of the metal oxide NWs such as ZnO, SnO_2 , In_2O_3 is normally attributed to oxygen vacancies, metal interstitials or incidental hydrogen(113-114). Temperature dependent measurements on single ZnO NWs have revealed that for $T > 100K$, the conductivity has an activation energy of 30 meV corresponding to the location of the shallow donor levels(115). In SnO_2 , doubly ionisable oxygen vacancies form levels with energies of 0.03-0.034eV and 0.14- 0.15eV below the conduction band edge, while hydrogen forms a donor state 0.05eV below the band edge(46-47). First-principle calculations has also shown the important role played by the tin interstitial and its attraction to the oxygen vacancy leading to formation of donor states(116).

Charge transport through single metal oxide NWs is very dependent on the properties of their surface due to their large area to volume ratios as well as their small Debye lengths. This implies

that the NW's conductivity could completely depend on the chemical processes transpiring on the surface of the NW. Simulation results also showed that the surface states control most of the electronic properties of the NWs(117). This has been widely exploited in the fabrication of gas sensors where the addition or depletion of majority carriers caused due to the adsorption of the gas molecules leads to measurable changes in the NW conductivity.

Compared with bulk and thin film materials, oxide NWs demonstrate enhanced sensitivity to the chemical environment owing to the large surface-to-volume ratio. In addition, the Debye length (also called Debye radius) is very comparable to the NW radius which makes the influences by surface processes even stronger on the electronic property, yielding superior sensitivity than their thin film counterpart(118).

Research have been conducted on the electrical properties of SnO_2 and ZnO individual nanobelts in different gas environment (vacuum, air, and oxygen) as a function of thermal treatment and suggest that the concentration of surface oxygen vacancies plays the most significant role in the oxygen adsorption and desorption dynamics, which, in turn, affect the carrier density in the nanobelts (33). Similarly, SnO_2 NWs exposed to high temperatures, inert or reducing ambient, demonstrate highly conductive properties which behave like heavily doped semiconductors or quasi-metals (119). When exposed to or thermal-annealed in oxygen, the NWs will transform into weakly doped semiconductors with high conductance activation energy. The charge depletion layer induced by surface adsorption completely controls the charge transport in single NWs, if the diameter of the NW is comparable to the depletion layer thickness. So methodologies need to be investigated in order to conserve the oxide NW properties in air.

However, previous reports were predominantly based on single NW devices with relatively small channel lengths ($<10\ \mu\text{m}$) (27, 33), or for devices fabricated using NW networks, the charge transport normally happens across distances less than the average length of the NW. This ensures that the electrical property of the ensemble is determined primarily by the NW and the NW-metal electrode interface. However, these outcomes are not representative of the scales desirable in large-scale electronics. In systems where the scale is bigger (such as used in macroelectronics), the charge transport is also determined by the NW- NW contact. On top of this, the intrinsic and extrinsic factors that influence the electrical properties of nanonets also need to be identified and examined, all of which will be discussed detailedly in this report.

Chapter 3

EXPERIMENT PROCEDURE

3.1 Nanowire Growth via VLS Process

Figure 3.1 Schematic illustration of the experiment setup applied to synthesize NWs through high temperature VLS growth

3.1.1 Pristine SnO_2 nanowire growth

As introduced in the previous section, the VLS growth method is widely used to grow NWs of different materials. One key feature of this synthesis is the promotion of anisotropic crystal growth using metal nanoparticles as catalysts. The general procedure is described below for the case of SnO_2 NWs growth. SnO_2 NWs were synthesized on Si (100) using a vacuum vapor transport. In general, a mixture of SnO_2 and active graphite powders (Sigma-Aldrich, both 99.9% purity with molar ratio 2:1) was used as source materials (carbothermal process) and loaded at the center of a quartz tube, as indicated in Figure 3.1. Temperature is rapidly increased to 900°C and the Si substrates with 2 nm Au as catalyst were placed downstream in a temperature zone around 720-760 °C. The temperature was held at the peak temperature for 15 mins (duration can be varied to alter the NW length) with argon carrier gas (oxygen

concentration in argon is adjustable) at a flow rate of 120 SCCM (standard cubic centimeter per minute), under pressure of 6.0×10^{-1} Torr [base pressure (before carrier gas released in) and growth pressure can also be varied to modify the intrinsic properties of NWs]. The system was slowly cooled to room temperature in vacuum environment. Tin oxide NWs were observed as white or light gray products on the Si substrates.

3.1.2. Doping of SnO_2 nanowires.

Antimony is one of the most commonly used dopant. The doping practice can be achieved in two ways. The mixture of $\text{SnO}_2 + \text{C}$ and Antimony pentoxide (Sb_2O_5 , 99.99%, Sigma-Aldrich. Molar ratio of Sn: Sb ranges from 100:0.5 to 100:5) was used in the first way as the source materials, with the remaining step is the same; In the other way, instead of loading the source material directly into quartz tube, Sn:Sb (powder, both 99.98%, Sigma-Aldrich) mixture with different molar ratio was loaded to a alumina boat first in order to prevent the random flow of the melting liquid when the metal mixture subjected to high temperature. Then the boat with source materials was loaded into the center of the quartz tube as mentioned above and following by the same growth procedure. The furnace temperature is set to 920°C . The 1st way was used in the present work unless mentioned.

Besides antimony, Nb and Ta were also adopted in the doping practice with the same growth conditions as way 1 (results are not discussed in the report).

Measurement of electrical conductivity and photoluminescence are discussed in Chapter 5.

3.2 Nanonet Formation through Contact Transfer and Device fabrication

Figure 3.2 Illustration of the physical transfer process used to fabricate aligned tin oxide NW arrays. The bottom part shows the patterning process of the active area.

After the growth of the tin oxide NWs, networks of them on another substrate can be prepared by contact transfer processes. The transferring process is shown in Figure 3.2. Briefly, the Si substrate with randomly grown SnO₂ NWs (donor substrate) was faced down against a precleaned Si₃N₄(200nm)/Si substrate (acceptor substrate) and slid ~ 10 mm to a certain direction with downward pressure. During the printing process, SnO₂ NWs were transferred to the Si₃N₄ substrate with the alignment along the sliding direction forming laterally aligned SnO₂ NW patterns. This technique utilizes shear force to effectively align the NWs, while van der Waal's force of attraction and other chemical binding interactions between the substrate and the NWs allow the NWs to anchor to the receiver substrate. This allows the formation of well aligned NW networks of high crystallinity even on unconventional substrates such as plastic and

glass. The density of the printed NWs is determined by the as-grown NW densities and can be increased by repeated printing. Besides, the size of NW area can be easily controlled by the size of donor substrate.

To achieve better management of the contact printing process, the following setup (Figure 3.3) was designed and 3-axis stage was used which allows the pressure control in x-axis while alignment and speed control in z direction.

Figure 3.3 Photo image of the transfer stage used in this project

Electrical characterization was done by evaporating 100 nm thick Al electrodes on top of the network by thermal evaporation using metal shadow mask with varied channel lengths (ranging from 75 to 500 μm for different purpose). SnO_2 NW density was fixed by exact control of the growth conditions during investigating the effect of the channel length.

As previously introduced, the control of initial Au film thickness and subsequent annealing conditions is shown to provide an effective method for controlling the size and density of

nucleation sites for catalyst-driven growth of SnO₂ NWs. Hence, the nanonet coverage can be modified by altering the density of the as-grown NWs.

On top of the simple contact-printing method, patterned photoresist can be adopted to define the active area, as shown in the bottom part of Figure 3.2. Cross wire networks can also be achieved by contact printing normal to the previous network. Lift-off of the photoresist completes the process as shown in the image.

3.3 Surface passivation

A surface passivation process was performed on the nanonet devices through drop casting a layer of Polystyrene (PS) (10 μ m) to prevent H₂O and O₂ absorption during air exposure. The devices were subjected to vacuum before the passivation for surface pre-cleaning.

Layer of SiO₂ (200 nm) deposited by Plasma-enhanced chemical vapor deposition (PECVD) at 400 °C was also adopted as the passivation layer. The high vacuum and temperature will function as vacuum annealing process which was expected to have pre-clean effect on the NW surface before the passivation layer was coated.

3.4 Characterization of as-grown NWs and nanonet based devices.

Various techniques were applied to characterize the as-grown SnO₂ NWs and the fabricated nanonet devices:

Thin film X-ray diffraction (XRD) was recorded on a XRD Shimadzu Standard instrument using Cu K α radiation. A JEOL JSM-7600F Field emission scanning electron microscope (FE-SEM) was used to observe the morphology of the SnO₂ NWs. Transmission electron microscope

(TEM) images were obtained with a JOEL JEM-2010 ELECTRON MICROSCOPE. X-ray photoelectron spectroscopy (XPS) was adopted to detect the dopant concentration in SnO_2 NWs. A He–Cd laser centered at 325 nm as the excitation source was used for photoluminescence PL measurements. Electrical properties were measured by the probe technique (ITP-6 probestation with vacuum chamber) using a Keithley 4200 source meter under the condition of both ambient and controlled environment [vacuum (10^{-6} Torr), low temperature (down to 77K), different gas environment (Ar, humid & dry air)] as shown in Figure 3.4. For photocurrent effect, light source from the cryogenic probe station microscope ($4\text{mW}/\text{cm}^2$) was used.

Figure 3.4 Illustration of electrical measurement setup.

Beside the above mentioned conventional tools, any other characterization system used will be discussed separately in the result and discussion section.

Chapter 4

RESULTS AND DISCUSSION

This chapter covers 4 sections. Section 1 describes the characterization of pristine nanonet devices including electron transfer mechanism, device passivation effect and device scale-up. The intrinsic and external factors affecting the nanonet behaviors including water vapor effect, surface defects and impurity doing are presented in Sections 2. Section 3 characterized the localized/trapped states in the NW-junctions through temperature dependent measurement. Section 4 details the interactions of oxide NWs with organic and inorganic materials and the application of NWs in DSSC.

4.1 Characterization of pristine nanonet devices and electron transfer mechanism in nanonet.

4.1.1 Physical characterization of as-grown nanowires and transferred nanonets

a. Usefulness of Chemical Vapor Deposition (CVD) growth

Figure 4.1 FESEM images of nanostructures grown via CVD approach (a) Vertically aligned ZnO NWs; (b) Comb-structured SnO₂ NWs; (c) Twisted structure of Zn-Sn-O NWs with inset shows the zoom-in image of Single wire; (d) CdS_xSe_{1-x} nanobelts.

Fig 4.1 exhibits various types of nanostructures grown via the same tube furnace (CVD) system. Obviously, chemical vapor deposition approach facilitates the diverse morphologies with different chemical compositions.

b. Tin oxide NWs

FESEM morphologies of the prepared NWs are shown in Figure 4.2a. Clearly, the as-grown NWs range from 80-120 nm and 20-40 μ m in diameter and length, respectively. The crystallinity

is confirmed by the SAED characterization and presence of well-defined X-ray diffraction peaks, indicating the tetragonal rutile structure of SnO_2 with lattice constants of $a = 4.738 \text{ \AA}$ and $c = 3.188 \text{ \AA}$. The as-grown NWs have a branched morphology typical of VLS grown SnO_2 NWs(120).

Figure 4.2 Physical characterization of as-grown tin oxide (SnO_2) NWs (a) SEM image of as-synthesized SnO_2 NWs. Left corner inset: SAED of the NW, right inset: single SnO_2 NW shows the length. (b) XRD pattern of the synthesized SnO_2 NWs with JCPDS21-1250 standard for comparison, (c) photoluminescence and (d) Raman spectroscopy spectra of SnO_2 NWs at room temperature.

A He-Cd laser centered at 325 nm was used as the excitation source for PL measurements and a strong orange luminescence peak is observed at $\sim 600 \text{ nm}$ from part c of Figure 4.2. This strong orange luminescence, which is normally not observed in tin oxide thin films, has been traced to the radiative recombination of surface-localized electrons and holes lying in the surface bands

created by surface bridging oxygen vacancies(121). Raman spectroscopy was also adopted to confirm the sample identification. Eigen frequencies of different vibration modes of Sn–O bonds can be detected by this light scattering technique and specific frequency values are expected for each stoichiometry. It has been reported that rutile SnO_2 is characterized by four fundamental Raman scattering peaks at $123 \text{ cm}^{-1}(\text{B}_{1g})$, $472 \text{ cm}^{-1}(\text{E}_g)$, $632 \text{ cm}^{-1}(\text{A}_{1g})$ and $778 \text{ cm}^{-1}(\text{B}_{2g})$ (122). While A_{1g} and B_{2g} are related to the expansion and contraction vibration mode of the Sn–O bonds, E_g is associated with vibration of oxygen in the oxygen plan(123). The intensity of B_{1g} phonon which corresponds to a vibrational motion of octahedra is very low that cannot be normally observed.

c. Tin oxide nanonets

Even though the as-grown SnO_2 NWs on the donor substrate are not ordered, contact printing yielded highly oriented NW networks (nanonets) with NW densities estimated at $\sim 0.3 \text{ NW}/\mu\text{m}^2$. Areal coverage of the nanonets is estimated at $\sim 35\%$ by imaging software (*Adobe*) (Figure 4.3). Cross-section image shows the well-formed single-layer thin film from contact printing (left corner inset of Figure 4.3). The areal density and film thickness can be increased by repeating layers through multiple contact printing processes. To be consistent, the data presented here are measured from transistors fabricated by a single contact printing process.

Figure 4.3 Physical characterization of transferred nanonets (a) FESEM images of aligned NWs. Inset on the up-right corner: FFT transformation of the image and the inset on the bottom-left corner: SEM image of the cross-section of nanonet. (b) Patterned NW arrays with zoom-in image on the up-right corner; (c) Nanonet with different densities of NWs exhibiting the corresponding transparency percentages; (d) Nanonet pattern formed on quartz (left), PET (right).

The alignment is confirmed with the Fast Fourier transformation (FFT) of the micrograph in up-right corner inset of Figure 4.3a. Presence of any alignment in a micrograph results in an elliptical image upon Fast Fourier transformation, with a *high* degree of alignment quantified by a *low* ellipticity angle(124-125). An ellipticity angle of $\alpha=20^\circ$ was observed in the SnO_2 nanonets, confirming a very high degree of alignment, which was also evident in the micrographs. Similar measurements on aligned ZnO NW samples prepared by contact printing yielded values of $\alpha = 10^\circ$ indicating that the branched nature of the as-grown SnO_2 NWs limits the level of alignment.

After contact printing, the length of the NWs (as grown: 20-40 μm) reduces to 5-15 μm . Consequently, the nanonet-FETs comprise $\sim$ 5-10 nanojunctions for devices with the smallest channel lengths of 75 μm and more than $\sim$ 25 nanojunctions for channel lengths of 175 μm .

Figure 4.3b illustrates the upgrading of the contact printing process to transfer NW arrays selectively onto a substrate. Photolithographical patterning of photoresist on the receiver substrate defines the open areas where transfer of the NWs can take place. Parallel NW arrays are shown after the lift-off process with very clear edge. This approach provides us the potential usage of the specific printing method in circuit fabrication.

With proper density control, the NW coverage can be fine-tuned from $\sim$ 25% to $\sim$ 90% with the visible light (@550nm) transparency floating between 80% to 70% (with NWs deposited on quartz) as shown in Figure 4.3c. Light scattering at the NW surface is believed to be the main source of the loss of transparency. It is worth noting that with the NW density approaching 90%, the nanonet will tend to form a continuous thin film layer.

The key advantage of contact printing can be seen in Figure 4.3d. Various substrates such as quartz (left) or PET (right) are used for NW transfer and ordered NW arrays were obtained with ease. The transferred nanonet demonstrated high transparency as shown in the right corner photo image against the NTU logo.

4.1.2 Electrical characterization of pristine nanonets device

Figure 4.4 (a) Transfer Characteristics of the FET indicating higher drain currents with smaller channel lengths. (b) Output $I_{DS}V_{DS}$ curves with $L=75 \mu m$. (c) ON/OFF ratio, threshold voltage and device mobilities vs. channel length. All the devices were tested in vacuum. (d) Transfer curves measured twice in air and vacuum showing the presence of threshold voltage shifts in devices measured in ambient. Effect of light illumination on transfer curve is also shown.(126)

In agreement with previous reports on single SnO_2 NW field effect transistors, the nanonet-FETs exhibit n-channel depletion mode behavior, with increasing on-currents for decreasing channel lengths and ON/OFF ratios ranging from 10^6 to 10^8 (parts a of Figure 4.4). From the output characteristics (part b of Figure 4.4), it may also be noted that the transistors show good saturation behavior. For the calculation of mobility, a parallel plate model is adopted to estimate the gate capacitance. It has already been shown that, for NW coverage in excess of 20%, the

effective capacitance value is very close to that obtained from the parallel plate assumption (within 80% of the measured actual value)(27). This arises from the fact that the NW array can effectively screen the field lines from the gate just as in a continuous film. Similar results on the effective capacitance for NW network devices have also been reported by J.A. Rogers and co-workers(127). An effective value of 90% of the parallel plate capacitance (corresponding to NW coverage of 35%) has been used for the subsequent mobility calculations. The saturation field effect mobility (μ_{sat}) ($(2I_{\text{DS}}L)/(0.9C_iW(V_G - V_{\text{Th}})^2)$) of the FETs was estimated from the slope of the transfer characteristics using the measured capacitance of the Si_3N_4 (C_i) 18.83nF/cm², 1 MHz). Channel width as defined by the Al electrodes was 4000 μm . The highest mobility (μ_{sat} , $L = 75 \mu\text{m}$, $W = 4000 \mu\text{m}$) was calculated to be 7.85 cm²V⁻¹s⁻¹. Mobilities in the linear regime (μ_{lin}) were estimated from the transconductance (g_m) (128) as $\mu_{\text{lin}} = g_m \times ((L)/(WC_iV_{\text{ds}}))$. For the smallest channel lengths the linear mobility (μ_{lin} , $L = 75 \mu\text{m}$, $W = 1000 \mu\text{m}$) was estimated at 3.5 cm²V⁻¹s⁻¹.

As anticipated, the device mobilities scale inversely with channel length (part c of Figure 4.4 and Table 4.1). The threshold voltage (V_{Th}), as determined by the intersection of the tangent of the transfer characteristics and the voltage axis, is $\sim 16 \text{ V}$ ($L = 75 \mu\text{m}$) and increases with increasing channel lengths. The increment in the threshold voltage (and the decreasing mobility) may be explained by the fact that longer channel length devices comprise increasing number of nanojunctions. As shown in part c of Figure 4.4, there is a slight reduction in the ON/OFF ratios of the nanonet transistor (10^8 to 10^6) with increase in channel lengths. This variation with the channel length is determined primarily by the higher saturation currents for the shorter channel lengths despite the slightly lower OFF currents for the larger channel lengths. The

generally low OFF currents in the nanonet transistors imply that the gold catalyst particles do not form percolation paths and play a minor role in determining the charge transport through the nanonets. The threshold voltage may be used to estimate the carrier concentration from the total charge, $Q_{\text{tot}} = C_g \times |(V_G - V_{\text{Th}})|$ (129) where C_g is the gate capacitance.

The carrier concentration (n_e) for the device with a cross-sectional area A , may be estimated by: $n_e = Q/(eAL)$. At applied gate voltages of 40 V, the carrier concentrations may thus be estimated as 2.75×10^{17} and $1.93 \times 10^{17} \text{ cm}^{-3}$ for channel lengths of 75 and 175 μm , respectively.

The relatively high mobilities obtained in these SnO_2 nanonet devices warrant further discussion. In contrast to the nanonets characterized here, previously reported studies on ZnO nanonet devices yielded mobility values of $\sim 0.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for channel lengths of 50 μm (128, 130). The superior performance of the devices reported in the present study may be traced to the intrinsically high mobilities in SnO_2 NWs as well as the high degree of alignment in the nanonets. The importance of alignment in dictating the performance of long-channel transistor (length of channel $>$ length of NW) has been previously explored in single-wall carbon nanotube networks (131). In the case of the long-channel transistor, the percolation threshold for a perfectly aligned network approaches infinity. Because of the branched nature of the as-grown SnO_2 NWs, there is a certain level of misalignment built into the system. This bridging of the NWs ensures multiple percolation paths and thus high drain currents. Another advantage of such network architecture is fault tolerance, which might come in play especially for applications that involve flexibility. Despite the high performance of these back-gated transistors, the fabrication of top-gated transistors is challenging at these device scales. With the large areas of the device ($W = 4000 \mu\text{m}$, $L = 75\text{-}175 \mu\text{m}$), the probability of a NW sticking out of the nanonet is high, thus

compromising gate dielectric integrity. Hence, additional planarization strategies have to be pursued such as pressing of the nanonet with ultra-flat Si piece to address this challenge.

The transfer characteristics of the as-prepared SnO₂ nanonet-FETs (tested in air) degraded severely upon repeated measurements. Part d of Figure 4.4 displays the characteristics of a transistor with $L = 100 \mu\text{m}$. Most noticeably, during the second $I_{\text{ds}}-V_{\text{gs}}$ sweep, the threshold voltage significantly increased from 12 to 25 V, whereas the mobility (μ_{sat}) decreased from 0.81 to $0.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The saturation regime also shifted and complete saturation was not observed even after biasing to $V_{\text{g}} = 40 \text{ V}$. The poor performance of the devices in air is also reflected in their clockwise hysteresis behavior indicative of charge trapping. Devices tested in vacuum show a hysteresis window of $\sim 3 \text{ V}$, whereas devices tested in ambient show a much wider hysteresis window of $\sim 18 \text{ V}$. This device performance degradation may be rationalized by the conversion of O₂ to O₂⁻ by withdrawing an electron from the SnO₂ NW surface. The large surface area of the nanonets facilitates surface adsorption of O₂, which subsequently leads to reduced carrier densities, increased depletion layer thicknesses, and precludes the formation of the saturation regime. When the same devices are tested in vacuum, they yield mobilities and threshold voltages of $6.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 18.1 V respectively and display stability of the transfer characteristics upon multiple $I_{\text{ds}}-V_{\text{gs}}$ cycles (part d of Figure 4.4). The decrease of adsorbents on the NW surface resulting from low-pressure increases the free carriers and reduces depletion layer thicknesses. These factors in turn reduce the junction barrier, thus reducing the energy needed for inter-wire charge hopping, effectively enhancing electron transport through the nanonets.

Similar to the vacuum effect, incident photon energy also results in desorption of oxygen ions on the NW surface, effecting a similar increase in electron mobility and a reduction in V_{Th} (part d of Figure 4.4). In addition, the incident photons may also play a role in releasing trapped electrons, enhancing charge transport through photon-energy assisted inter-wire hopping. Upon capturing the holes generated under the illumination, the negatively charged oxygen ions will be able to detach from the NW surface which resulted in the thinning of the surface depletion layer. Hence the number of electrons to transport inside the NWs will increase, causing the rise in the both photocurrent and electron mobility inside the nanonet (Table 4.1).

4.1.3 Mechanism of electron transfer in Nanonet

Figure 4.5 Schematic illustration of the band structure and electron transfer in (a) single crystalline thin film, (b) polycrystalline film and (c) NW networks. In nanonet scheme, the depletion region becomes smaller under vacuum or illumination. (a) and (b) are reproduced from (38).

In all the format, the thickness of the depletion layer is calculated through the following

equations $T_D = L_d \sqrt{eV_s / kT}$, with $eV_s = e^2 N_{ss}^2 / 2\epsilon N_D$ where L_d is Debye length, N_D is the

density of donor states in the bulk N_{ss} is net surface density of charged states per energy unit.

Raising the density of donor states (N_D) or reducing the density of surface charge states will result in the narrowing of depletion layer hence enhancement of the conductivity.

Similar to poly-crystalline film, the transport mechanism of electrons in the nanonets, as illustrated in Figure 4.5, comprises either intra-wire or inter-wire (hopping) transport, with the latter resulting in a loss of kinetic energy of the electrons. It has been reported that the semiconducting nature of a number of transition metal oxides is strongly determined by oxygen vacancies(33). However, the adsorption of chemical species such as oxygen molecules and OH-radicals cause a change in surface states that affect the width of the conducting channel. Adsorbed oxygen molecules may form oxygen ions such as O_2^- that extract electrons from SnO_2 , resulting in a depletion of the charge carriers in the NW. In addition, surface adsorbed H_2O and OH- groups tend to accumulate electrons to form a positive space charge, which may further affect the depletion layer(132). The depletion regions in the NWs act as obstacles that hinder the electron transfer from one NW to the other and delay the turn-on of the nanonet transistors. Both scanning surface-potential microscopy (SSPM) and gas-sensing measurements indicate that the junction resulting from crossing the quasi-1D nanostructures dominates device properties(133) and leads to the decrease in electron mobility as well as an increase in the threshold voltage. This effect is more pronounced in longer channels due to the increasing number of nanojunctions. The threshold voltages increase from 16 to 23 V with channel lengths

increasing from 75 to 175 μm (part c of Figure 4.4). The high concentration of oxygen molecules in the ambient leads to a further widening of the depletion region and a higher gate bias is required for the accumulation of free carriers thus resulting in a higher ambient V_{Th} .

A point to note is that tunneling transport can be present and serve to modulate the effective energy barriers that extracted from measurement. However, it is difficult to isolate the different mechanisms.

a. NWs with higher conductivity

It was later found out that nanojunctions can also have positive effect in high conductive NW networks. In this process, NWs with high carrier density (by improving the NW crystallinity in the later stage of the project through lowering the NW growth pressure) was used and devices were made with channel lengths ranging from 150 to 500 μm . Device performance is shown below in Figure 4.6.

Figure 4.6 Transfer characteristics of nanonet FETs with channel length ranging from 150-500 μm . NWs used here are highly conductive.

The calculated carrier mobility is 10.1, 21.7, 35.6, 46.3, 48.5, 52.3 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for the devices ranging from 150 to 500 μm , respectively. It indicates that the enormous scattering effect is greatly reduced though increasing the number of junctions which may be attributed to elevated number of localized/trapped states at the junction sites [This issue will be further discussed in the low temperature section].

b. Nanonets with higher density

Figure 4.7 Transfer characteristics of nanonet FET devices (a) with diverse NW densities. (b) high density nanonet with different channel lengths, inset is the output curves of device with $L=80 \mu\text{m}$.

The same effect happens to the devices with higher NW density. It is interesting to note that with NW density approaching 90%, the nanonets transferred will tend to form a continuous thin film layer. This can be inferred from the FESEM image as previously introduced and the electrical characterization of nanonet FET in Figure 4.7a. The OFF current is significantly higher for nanonet with high density and decrease with the reducing of network density. In this sense, higher nanonet density won't necessarily promise a better electrical performance since it will greatly shift the threshold voltage to very negative side which degrades the field effect. Lower density nanonet will provide the best OFF current, however, the low density will limit the

carrier density and electron mobility hence the ON current level. For this particular range of channel lengths, medium density sample gave the best electrical performance and was adopted for the following experiment.

Meanwhile, while the devices made by low to medium density nanonet are still following the model we earlier proposed, the high density ones may not be that obvious. This phenomenon can be explained by the theory of junction in series and parallel which can be similar to the resistors in circuit. The overall resistance of the active area will be significantly reduced due to the large amount of parallel junctions existing in high density nanonet devices, which can be solved by simply enlarging the channel lengths to raise the series resistance as previously discussed.

4.1.4 Passivation of the NW networks

a. Polystyrene (PS) as passivation layer

Figure 4.8 Transfer curves of the nanonet devices with and without passivation layer of polystyrene (PS). In the consecutive measurement of with PS, the transfer characteristics is invariant showing the stability of device in air. (b) Output curves of nanonet device measured in ambient with passivation. For all devices, $L = 100 \mu\text{m}$.

Because of the sensitivity of the SnO_2 NWs to the ambient, passivation strategies involving the deposition of a polymeric overlayer were pursued. The effect of passivation with polystyrene (PS) on device characteristics of SnO_2 nanonet FETs is visible in Figure 4.8 and Table 4.1. The sealing of the nanonets by the polystyrene layer improves the output characteristics, as well as eliminates the threshold voltage shifts associated with devices tested in ambient. Similar to devices tested in vacuum, the improvement in the passivated device performance is attributable to reduced oxygen- (and OH^-) NW interaction. The only decrement in device property was the rise in the OFF current possibly caused by mobile interfacial charges that may remain trapped in the polystyrene passivation. Another possibility is the formation of an additional leakage path through the upper PS layer, which could increase the OFF current. The charge carrier mobilities in the passivated transistors are not as high as the ones measured in vacuum due to the residual oxygen adsorbed on the NW surface prior to the passivation process.

Table 4.1 Summary of the Device Mobilities at various conditions and Channel Lengths

Devices	Channel Length (μm)	Effective-Saturation Mobilities ($\mu_{\text{sat-eff}}$)			
	Working environment	75	100	125	175
W/o PS layer	Ambient air	1.06	0.70	0.45	0.33
	Vacuum	7.85	6.48	3.80	2.37
	Vacuum with light	9.70	9.07	6.30	3.99
W/ PS layer	Ambient air	4.39	3.76	1.93	1.29

b. SiO_2 as passivation layer

The same effect was shown on devices with SiO_2 passivation deposited by PECVD (Figure 4.9). The device presented here was fabricated in the later stage of the project with improved device design and NW quality. The less obvious effect when devices subjected to air is due to the increase bulk carrier density which reduces the thickness of surface depletion region. It is

apparent that with the passivation layer, the devices exhibited superior stability and the effect was greatly enhanced compared with PS coating due to the vacuum annealing process prior to PECVD deposition and the compact interface between two materials.

Figure 4.9 The transfer and output characteristics of devices before (a-b) and after (c-f) SiO_2 passivation deposited by PECVD. SEM image of SnO_2 with SiO_2 passivation is shown as inset of c.

4.1.5 Large-scale device fabrication and uniformity testing.

FETs on the area of $1 \times 1 \text{ cm}^2$ substrate were fabricated and device uniformity were tested as shown in Figure 4.10. To compensate the design, the high conductive NW networks were transferred on to $\text{SiO}_2/\text{P}^{++} \text{ Si}$ substrate and the devices with $L=500 \mu\text{m}$ were fabricated. A 100nm SiO_2 passivation layer was deposited on top of the devices via PECVD.

Figure 4.10 (a) Photoimage of large-scale ($1 \times 1 \text{ cm}^2$) nanonet devices, where the active areas are the white, reflecting squares as shown; (b) Mask-design used to characterize the electrical uniformity of the devices.

Figure 4.11 (a) (b) Comparison of transfer curves of devices with same dimensions (from 4 corners); (c)(d) histogram plots of performance scattering

The uniformity of nanonet transferred in large-scale is testified by characterizing devices from all the 4 corners. As seen in the histogram plots (Figure 4.11), the devices exhibited high electrical consistency with the variance suggesting the feasibility of our fabricated nanonet in large-scale application.

4.1.6 Extending the NW transfer technique to other type of nanowires.

a. ZnO nanonet devices

Figure 4.12 (a) As-grown ZnO NWs with the zoom-in image as inset; (b) ZnO NW network fabricated through contact printing. (c) Transfer characteristics of ZnO nanonet transistors ($L = 75 \mu\text{m}$, $V_{DS} = 40 \text{ V}$). (d) Output characteristics of ZnO nanonet transistor showing good saturation characteristics.(134)

Figure 4.12 shows the application of a contact printing approach to ZnO NWs to form NW network transistors. The ZnO NWs were grown using standard VLS techniques prior to contact-printing on to a silicon nitride substrate. Contact printing method allows a more ordered structure of ZnO NW networks with a higher leveled alignment. The scenario for charge transport in NW networks is shown as well. Similar to SnO_2 NW networks, results on channel length scaling have also been reported for ZnO NWs. In the transistors illustrated in Figure 4.12c, it is apparent that the ZnO NW network transistor ($\mu = 0.0145 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) has poorer charge transport properties than the SnO_2 one ($\mu = 7.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This could stem from multiple factors. The average length of the ZnO NWs (6–8 μm) after contact printing is lower

than that of SnO_2 (10–15 μm), implying a larger number of NW –NW junctions that act as bottlenecks for the electron transport between the source and drain electrodes. Differences in the NW network density may also play a role. The lower density of NWs in the ZnO network (0.2 NWs per μm^2) reduces the number of charge-transport paths, resulting in lower mobility devices.

b. $\text{CdS}_x\text{Se}_{1-x}$ nanobelt networks

Figure 4.13 (a) SEM image of the horizontally aligned $\text{CdS}_x\text{Se}_{1-x}$ nanonet. Inset: schematic illustration of the nanonet-FET. (b) Output characteristics of $\text{CdS}_{0.8}\text{Se}_{0.2}$ at V_{GS} from 5 to 30 V. (c) Transfer characteristics of $\text{CdS}_{0.8}\text{Se}_{0.2}$ nanonet-FET under light illumination with different intensities. (d) Photo-response behaviour of $\text{CdS}_{0.8}\text{Se}_{0.2}$. (135)

A contact printing method was also employed here to align the $\text{CdS}_x\text{Se}_{1-x}$ nanobelts. Figure 4.13a shows the SEM image of the horizontal aligned nanonet-FET fabricated from $\text{CdS}_{0.8}\text{Se}_{0.2}$ nanobelts. The typical output curves are shown in Figure 4.13b, with V_{GS} increasing from 5 V to 30 V in steps of 5 V. The nanonet-FET exhibits an obvious gating effect and typical n-channel depletion mode behaviour with good saturation. The photo-response (or photocurrent) behaviour is revealed in Figure 4.13c&d. The $I_{\text{DS}}V_{\text{GS}}$ transfer curves ($V_{\text{DS}} = 20$ V) under different light intensities (1, 3, 5 W/m^2) are shown in Figure 4.13c. It is obvious that the threshold voltage (V_{Th}) left-shifted significantly with the increase of the illumination intensities. Despite an increased saturation current with the intensities, the ON-OFF ratio declined from 5.8×10^5 to 2.9×10^4 since the increase of OFF current is more prominent. The high number of photo-generated electrons under intensified illumination made the gate voltage effect less dominant which resulted in a less steep curve in the $I_{\text{DS}}V_{\text{GS}}$ figure, reducing the device mobility.

Figure 4.13d shows the photo-response of the $\text{CdS}_{0.8}\text{Se}_{0.2}$ nanonet to the normal white-light source as a function of time. The bias voltage was fixed at 20 V and the applied light illumination was 50 W/m^2 . Evidently, the photocurrent increases dramatically to 2.8 μA in a very short period ($< 2\text{s}$) after the sensor was exposed to the light source while the current was only at the level of nA under dark condition.

As presented, a large scale $\text{CdS}_x\text{Se}_{1-x}$ nanonet-FET device has shown an obvious gating effect and pronounced photosensitivity. The $\text{CdS}_x\text{Se}_{1-x}$ nanonet based photosensor exhibits fast response to normal and weak white light. The $\text{CdS}_x\text{Se}_{1-x}$ ternary alloyed nanobelts with tunable optical properties have potential application in photoelectronic devices.

4.1.7 Summary

Highly oriented SnO₂ nanonet field-effect transistors were fabricated by direct-contact printing and their electrical properties were characterized under various environments. These nanonet devices displayed a good device characteristic yielding high charge carrier mobilities even at large scales. The surface state dependent electron mobility inside the nanonets was studied by characterizing the FET in vacuum, ambient, as well as under illuminated conditions. Adsorption of oxygen leads to the formation of a depletion layer on the surface of the NW which serves as energy barrier at the junctions, affecting the electron transport properties in these nanonets. Stabilization of the electrical properties of the nanonets in ambient conditions was obtained by passivating the surface with a polystyrene and SiO₂ overlayer. The large scale NW networks provide advantages in flexibility and fault tolerance which makes it amenable for applications in flexible electronics and allow the possibility of fabricating low-cost, transparent, high-performance macroelectronic devices.

4.2 The intrinsic and external factors affecting the nanonet behaviors

4.2.1 Surface defects and environmental effect.

In real life applications, one of the critical factors that would determine the electrical performance of such metal oxide nanostructures is its response to ambient conditions. To our best understanding, there are few reports detailing the dynamics of water vapor and oxygen interaction on metal oxide NW network field effect transistors. Understanding the response of nanonet to the surrounding environment, especially the origin of hysteresis in the dual sweep which can degrade the transistor performance will be essential for practical applications.

As shown in the previous section(38), it has been widely investigated that adsorbed oxygen molecules on SnO_2 NWs may form oxygen ions such as O_2^- which extracts electrons from SnO_2 , thereby reducing the electron mobility and current generation in the devices. However, vacuum treatments or photoinduced desorption can reverse the process.

On the other hand, the influence of adsorbed water vapor on the optoelectronic properties of SnO_2 NWs has not been clearly established. Although adequate work has been done on the tin oxide surface researches, the conclusions were mainly based on the gas sensing format by by evaluating the changes in electrical characteristics (I-V characteristics) of thin film or nanostructures. On top of this, we noticed that even though water effect is claimed to be reversible, a large time constant of the order of around 1 h is needed(136).

Hence in this section, we have studied two varieties of SnO_2 NWs grown under differing oxygen concentrations (during VLS process). The effect of water vapor and oxygen on the

optoelectronic properties of the FETs were studied by subjecting the devices to different working environments.

While the other growth parameters are held constant, the section here used two different transport gases, pure Ar (denoted as 0%O₂) and 0.5% O₂/Ar pre-mixed gas (denoted as 0.5%O₂) for the growth. [Excessive oxygen in the carrier gas will oxidize the carbon in the source material which will retard the carbothermal reduction process]. The devices were characterized under the following conditions: Humid air (~70% water content), pure dry air (mixture of N₂/O₂, water content less than 5ppm), pure Ar, premixed 5%O₂/Ar and vacuum (1×10^{-2} Torr). Halogen light source with the intensity of 4mW/cm² were used for illumination in this testing process.

a. Characterization of the NW surface defects

Figure 4.14 (a) (b) FESEM images of the as grown SnO_2 NWs; (c) XRD characterization of the NWs; (d) PL characterization of the NWs.

The NWs grown from 0% and 0.5% O_2 /Ar transport gas mixtures are shown in Figure 4.14a&b. The NWs have diameters ranging from 60-80 nm for both conditions. However, it is obvious that longer wires with more uniform distribution and higher density are present in the 0.5% O_2 sample. Even though less oxygen is provided during the growth of the first sample (0% oxygen), XRD patterns in Figure 4.14c confirms that there are no other phases such as SnO or SnO_{2-x} formed. Photoluminescence measurements revealed a strong orange luminescence peak at ~ 600 nm from both samples as indicated by Figure 4.14d. Since this strong orange luminescence has been attributed to the radiative recombination of surface-localized electrons and holes lying in the surface bands created by surface bridging oxygen vacancies(121), it can be used as an indicator of surface defect density. It is obvious that with the increase of O_2

concentration in the carrier gas mixture, the intensity of the PL peak decreased dramatically for the major peak centered at 600nm as well as the minor peak ranging from 900 to 1000nm, despite the higher NW density for 0.5% O₂ sample. The lower energy photoemission band (900-1000 nm) may indicate there is possibility that electrons existing at this level and occupation of shallower donor level from which carriers can be excited relatively easier in the 0% O₂ grown samples.

Figure 4.15 HRTEM images of the as grown NWs with the SAED insets (a) 0 % O₂ /Ar grown; (b) 0.5% O₂ /Ar grown.

The HR-TEM images with the respective SAED pattern as inset are shown in Figure 4.15. SnO₂ NW grow along the [101] direction with a clear lattice fringe of 4.737 and 3.186 nm, which demonstrates that tin oxide NW is a single crystal with rutile structure. It is notable that for 0% O₂ grown NWs (Figure 4.15a), a 1.4 nm thick defect layer is present on the wire surface, while the surface defect layer thickness is only limited to 0.5 nm for the NWs grown from 0.5% O₂ /Ar mixture. This is consistent with the PL characterization which indicates that the

incorporation of sufficient oxygen during NW growth will significantly reduce the oxygen defects on the surface.

b. Electrical characterization of the environmental effect

Figure 4.16 (a) FESEM image of the aligned tin oxide NW networks, scale bar: 5 μm ; (b) transfer characteristics of nanonet FETs in humid air under different V_{DS} ($W:L=3000:100 \mu\text{m}$); (c)(d) The output characteristics of nanonet FETs in humid air.

Nanonets were formed in order to test the optoelectronic properties of these SnO_2 NWs (0% & 0.5% O_2). FE-SEM images of the transferred nanonet are shown in Figure 4.16a. Highly ordered networks were obtained even though the as-synthesized NWs on the donor substrates are random. Consistent with the as-grown NW density, the network of 0.5% O_2 NW showed a

higher surface coverage ($\sim 35\%$) than the 0% O_2 network (25%). In spite of the different densities, FETs fabricated from both the networks displayed typical electrical behavior. The transfer characteristics of the devices measured in humid air ($\sim 70\%$ humidity) are shown in Figure 4.16b. Obviously, both of the devices showed n-type semiconducting behavior when the drain voltage is low ($V_{DS} = 1\text{ V}$), with a clear turn on voltage indicating the formation of conducting channel and increase in drain current at higher positive gate voltages. On the other hand, increasing the drain voltage (V_{DS}) to 20 V results in nearly linear curves for the two transistors. These high currents are indicative of the remarkable amount of free carriers which are formed under interaction with the surrounding environment, greatly screening the gate voltage effect.

To examine the source of the extra free electrons from the ambient, different gas environment [pure Ar, Ar+5% O_2 , dry air and vacuum (1×10^{-2} Torr)] were adopted for the characterization. The results are displayed in Figure 4.17c&d, $V_{DS}=20\text{V}$ for all cases. The measurement chamber was gradually purged with the selected gases with the simultaneous measurements of the electrical characteristics.

Figure 4.17 (a) Illustration of the electrical behavior of nanonet-FET when devices were subjected to dry air (0% O_2 NW) subsequent to testing in humid air; inset shows continuous measurement of the device response on re-exposure to humid air. Each voltage sweep lasts 40s.; (b) Performance of nanonet-FET in 5 different testing environments namely humid air, pure Ar, Ar+5% O_2 , dry air and vacuum (1×10^{-3} Torr). (c) Output characteristic in dry air (0% O_2); (d) shows same characterization as (a) but 0.5% O_2 NWs were used.

As shown in Figure 4.17a, both the ON and OFF current decreased significantly with the influx of dry air. The OFF current reduces by about 8 orders of magnitude while the corresponding reduction for the ON current is only 2 orders, which ensured the device has a clear n-type semiconducting behavior with an ON/OFF ratio of 10^6 . The threshold voltage right shifted to -1.5 V with the electron density reduced to $2.55 \times 10^{12} \text{ cm}^{-2}$ at $V_{GS} = 20\text{V}$ [sheet carrier density calculated as $n_s = (1/q) C_{OX} (V_{GS} - V_{TH})$, where C_{OX} is the capacitance of the gate dielectric]. In

addition to changes in the drain current, hysteresis also diminishes with increasing amount of dry air. The transfer curves as performed under various atmospheric conditions are displayed in Figure 4.17b. Devices tested in all artificial environments (pure Ar, Ar+5%O₂, dry air and vacuum) which eliminated water vapour have well defined transfer characteristics and low hysteresis. Dry air resulted in the lowest current (both ON and OFF) and largest hysteresis ($V_{TH(back)} - V_{TH(forward)} = 7.5V$) while vacuum environment gave the smallest hysteresis ($V_{TH(b)} - V_{TH(f)} = 3.2V$). 5%O₂/Ar showed a bigger hysteresis ($V_{TH(b)} - V_{TH(f)} = 6.0V$) than pure Ar ($V_{TH(b)} - V_{TH(f)} = 4.8V$) which indicates both H₂O vapor and O₂ adsorption contribute to the hysteresis. Adsorbing and desorption of O₂ on the surface traps could be responsible for the large hysteresis when water vapor is absent. Reducing the concentration of O₂ will bring down the hysteresis even further, explaining the characteristics of the transistor in vacuum.

The increase in NW network conductance under humid conditions due to additional charge carriers could either be attributed to electron donation from an adsorbed OH group through the proposed reaction: $H_2O^{gas} + Sn_{Sn} + O_O \leftrightarrow (Sn_{Sn}^{\sigma+} - OH^{\sigma-}) + (OH)_O^+ + e^-$ or attributed to the reaction between the hydrogen atom and the lattice oxygen which results in oxygen vacancies: $H_2O^{gas} + 2Sn_{Sn} + O_O \leftrightarrow 2(Sn_{Sn}^{\sigma+} - OH^{\sigma-}) + V_O^{2+} + 2e^-$ (136-137). In addition, it is noted that in this NW network system, both the water vapor desorption and recovery process is much faster than previously reported in literature (on the order of 1 hour(136)). As Figure 4.17a exhibited, dry air took less than 5 cycles (around 40s per cycle) to displace the attached water vapor and reveal an ON/OFF ratio of 10⁶. The devices degraded to their original status within 3 cycles after exposure to humid air. One obvious reason is due to the large number of surface defects in the as-grown NWs and the large surface area presented in the as-fabricated devices. Another

source is explained by the manipulation of NW-NW junctions. Figure 4.18 illustrated the effect of H₂O adsorption and desorption. As indicated, the generation of free electrons resulted from the water adsorption will not only reduce the depletion layer of individual NWs according to the equation $W = L_d [e^2 \cdot N_{ss}^2 / 2 \varepsilon \cdot N_D \cdot k \cdot T]^{1/2}$ where N_D is the number of donor states (L_d is Debye length, N_{ss} is net surface density of charged states per energy unit, e is the elementary charge, k the Boltzmann's constant, T the operating temperature in K), but will also tend to reduce the energy barrier at the nano-junctions as suggested by the relationship $\Phi_b \propto 1/N_D$ (138). It is reported that a downward bending of 0.1 eV could be observed for water adsorption on stoichiometric SnO₂ (110) surfaces(139). As suggested by previous studies, electron transfer through junction barriers is the dominant mechanism during electron transport within the NW network (due to the high electron mobility in individual wire, the conducting path within a NW can be treated as “short circuit” between the barriers at the nanojunctions) and reduction of the energy barrier will result in a significant increase of the amount of free carriers flowing within the nanonet. These two advantages support the potential application of these structures as high-sensitive, fast response water sensor. (Similar but less obvious result is obtained for 0.5% O₂ nanonet devices as shown in Figure 4.17d).

Figure 4.18 (a) The change of depletion layer and height of energy barriers upon water vapor adsorption and desorption. (b) Schematic band diagram of SnO_2 with extra free electrons contributed by water vapor adsorption, under negative bias (left) and positive bias (right). The free electrons contributed by water vapor lift-up the Fermi level and significantly increased the carrier density in the channel for both cases.

Despite similar behavior under exposure to water vapor, different photocurrent responses were observed for the two variations of NW devices as shown in Figure 4.19. For devices working in humid air, the photocurrent response is not obvious for both the devices. This can be attributed to the large amount of free electrons generated by water vapor which may affect both gate

voltage and photocurrent effect. The decrease of the current with time may due to the electron traps executed by either oxygen molecules or the NW surface defects.

Figure 4.19 The photocurrent response for the two types of NWs (a)(c) 0% O_2 nanowire; (b)(d) 0.5% O_2

When devices were illuminated with light, 0% O_2 grown nanonet devices subjected to Ar, 5% O_2 / Ar, dry air and vacuum (Ar and 5% O_2 / Ar gas environment which are not shown here have the same effect of vacuum environment) showed obvious increase in current as can be seen in Figure 4.19a&c. Both of the ON and OFF current increased together with the left-shift of the threshold voltage. Using the equations as introduced in the previous section, it showed that the

electron mobility increased from 2.25 to 2.8 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for the devices in dry air, and from 2.34 to 2.96 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for the devices in vacuum. The sheet free carrier density also increased accordingly. However, referring to the time variable, it is worth noticing that the general trend for 0% O_2 is always decreasing regardless of dry air, Ar or even vacuum environment which can be possibly attributed to the different surface adsorbing/desorbing energy.

Compared with 0% O_2 nanonet devices, 0.5% O_2 showed very small enhancement when subjected to dry air and vacuum as shown in Figure 4.19b& d. The increasing current with time is compliant with the relative less defects presented on the surface as shown by TEM and PL. Releasing and re-adsorbing of the O_2 molecules on the wire surface makes the current increase more prominent for devices in dry air than the one in vacuum when devices were under illumination.

4.2.2 Tuning of the electrical properties of nanowires by doping

The aforementioned observations provide several opportunities to increase the current of nanonet devices. It has been discussed in previous section that the resistance of inter-wire junctions decreased by reducing the channel length, increasing the length of NWs or improving the nanonet density. Another way would be to increase the number of electron carriers within the NWs. As introduced in the literature review section, doping plays a critical role in tuning the electrical properties of the metal oxide materials and introduction of Sb into tin oxide allows the modulation of the electrical properties from semiconducting to metallic, depends on the concentration of the dopants.

Hence in the following section, we studied the antimony doping effect on the electron transportation in tin oxide nanonet transistors. Tin oxide NWs were grown through chemical vapor deposition with varies concentration of antimony in the raw material. Photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS) confirmed the existence of Sb dopants while significant up-shift of OFF and On current in transfer curves indicates the drastic increase of carrier density inside the nanonet. However, the huge amount of electrons flowing in the nanonet will also degrade the gate voltage control. This change of electrical behaviors is attributed to the attenuation of NW surface dielectric layer and the reduction of energy barrier at the nano-junctions.

Growth of NWs still follows the same way with minor modification on the source used. Instead of pure SnO_2 , Sn (SnO_2+C):Sb (Sb_2O_5 powder, 99.99%, Sigma-Aldrich) mixture with different molar ratio (ranging from 100:0.5 to 100:5) was used. The characterization still follows the same way except x-ray photoelectron spectroscopy (XPS) were added for dopant concentration analysis.

a. Physical characterization of doped NWs

Figure 4.20 SEM image of (a) a representative as-grown sample; (b) Sb-doped sample. (c) XRD patterns of three samples, insets show the large magnitude of (110) peaks. (d) XPS spectra of the doping samples, insets show the large magnitude of Sb 3d peaks.

While pristine SnO₂ NW exhibit milk-white color on Si substrate, Sb-doped SnO₂ shows slightly pink-white and the pink element tended to be more dominant with the increasing concentration of Sb. FE-SEM morphologies of the prepared NWs are shown in Figure 4.20a&b. The diameter of as-grown NWs ranges from 80-120 nm for both of the two and there is no remarkable dissimilarity between the pristine and doped NWs (2% as in raw material) from the morphology images. The only visible difference is that tiny aggregates formed in the doping sample (as marked by the red circle) with the reason is unclear so far; however, the composition is still tin oxide through Energy-dispersive X-ray spectroscopy (EDX) studies. The crystallinity is again confirmed by the presence of well-defined X-ray diffraction peaks that can be indexed according

to the tetragonal rutile structure of SnO_2 . There is no trace of any other expected secondary phases such as Sb clusters, Sb_2O_3 and other forms of Sn oxides to be seen in the pattern for all the samples. This may due to the relative similar size of this Sb^{5+} compared with Sn^{4+} and the fact that the doping concentration is very small. Although no significant shift was observed from the XRD patterns, the full width at half maximum (FWHM) of the main peak (110) reveal a slightly decreasing trend from 838 arc sec to 807 arc sec with increasing the dopant concentration, as shown in the insert of Figure 4.20c. XPS was carried out to detect the doping concentration of antimony in SnO_2 NWs. As shown in Figure 4.20d, two weak peaks at 530.4 and 539.9 eV corresponding to Sb 3d core levels are exhibited in addition to the Sn and O signals, indicating that antimony is indeed incorporated into the SnO_2 NWs. The corresponding contents of Sb were calculated through Gaussian fitting to be ca. 1 at. % for sample 2 (raw material ration Sn:Sb=100:0.5) and 1.5 at. % for sample 3 (raw material ration Sn:Sb=100:2.0), as labeled and displayed in the inset of Figure 4.20d.

Figure 4.21 Photoluminescence spectra of tin oxide NWs doped with diverse ratio of antimony (raw material ratio). The PL spectra were zoomed-in at the emission wavelength region 850-1000 nm.

He-Cd laser (325 nm) was used as the excitation source for PL measurements and a strong orange luminescence peak is observed at ~ 600 nm (Figure 4.21). We know that this orange peak has been traced to the radiative recombination of surface-localized electrons and holes lying in the surface bands created by surface bridging oxygen vacancies as previously introduced(121). It is obvious that with increasing dopant concentration of antimony, the intensity of the major PL peak centered at ~ 600 nm decreased dramatically and that of the minor peak centered at 900 nm increased. This may indicate that the cooperation of antimony inside the NWs can significantly reduce the surface defects and enhance the shallow donors at the higher energy closing to the conduction band. Band structure calculations for Sb doped SnO_2 have suggested the formation of a Sb 5s like band in the SnO_2 band gap with a free electron-like character at the Γ - point which may be the source of shallow donor at 900 nm(38), which results in a significant increase of free carriers and hence the conductivity.

b. Electrical characterization of doped NWs via FET

From the lattice point of view, Sb^{5+} will substitute Sn^{4+} in the compound and contribute one extra free electron. Thus, adding specific amount of antimony will moderate the electrical behaviors of SnO_2 NW from semiconducting to metallic-like conducting behavior. Sb doped nanonet FETs were fabricated through the same strategy with the electrical characteristics presented in Figure 4.22.

Figure 4.22 (a) Typical output I_{DS} - V_{GS} characteristics curves. Inset shows the diagram of the nanonets FET configuration. Typical output I_{DS} - V_{DS} characteristics curves of (b) sample 1, (c) sample 2, and (d) sample 3.

Figure 4.22a shows the typical I_{DS} - V_{GS} transfer curves and the inset illustrates the configuration of field-effect transistors made from nanonets with the output characteristics shown in Figure 4.22b-d which display the typical output characteristics curves for nanonets with 0, 0.5 and 2% Sb (raw material ratio), respectively. Evidently, all the nanonet samples show semiconductor behavior and the gating effect is pronounced. The positive gate voltage results in the enormous rise of source-drain current, indicating that all the nanonets are n-type semiconductors. Clearly the magnitude of ON current level increases with an increase of Sb doping. However, the gate voltage effect becomes less dominant with increase of the dopant concentration, as revealed by the off current increasing or lessening of the increasing steps of output current with increasing

gate voltage (Figure 4.22b-d). The diminishing of gate effect is attributed to the significant increase of electron carrier density induced by antimony doping.

The calculated electron mobility for 0, 0.5 and 2% doping (raw ratio) are 10.5, 6.6 and 4.8 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ while the carrier density is estimated to be 0.6, 17.8 and 53.4 cm^{-3} , respectively. The DC conductivity of the nanonets could be estimated from the $I_{\text{DS}}-V_{\text{DS}}$ characteristic curves ($V_{\text{GS}}=0$) and the corresponding values of different samples are calculated to be ca. 567, 1911 and 2612 $\Omega^{-1}\text{m}^{-1}$. All the values of electron mobility, carrier density and conductivity of these nanonets calculated through this contact method are listed in Table I for further comparison with those obtained from non-contact method which will be discussed in the following part.

Figure 4.23 (a)(b) The $I_{\text{DS}}V_{\text{DS}}$ output curves when $L=2000 \mu\text{m}$ and $120 \mu\text{m}$ respectively while $W=20 \mu\text{m}$, devices are with 5% Sb doping.

Figure 4.23 a&b shows the electrical output curves of 5%Sb (by molar ratio) doped SnO_2 nanonet FET's. It is worth noticing that the width of electrode here is only $20\mu\text{m}$, which indicates much fewer channels will be present for electron transferring. The different characteristics of the $I_{\text{DS}}V_{\text{DS}}$ output curves for various channel lengths suggest that the metallic-like property was exhibited for individual NW (equals to devices with smaller channel length)

which is consistent with the literature; while for the devices with longer channel length ($> 500 \mu\text{m}$, consisting of more than 50 NW junctions), semiconducting property was shown. This result reconfirms the significant role of nano-junctions in the electron transfer in nanonets. As the NWs and junctions are connected in series, the effective mobility of the nanonet medium can be approximated as $1/\mu_{\text{eff}} = 1/\mu_w + 1/\mu_j$, where μ_w and μ_j are the mobility in the NW itself and in the junction barrier, respectively. As reported, electron mobility in single NW device with antimony doping can go up to $550 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, thus it is reasonable to assume that the overall mobility would be limited by the junction barriers when the devices are with very large channel length. This explains the metallic-like behavior for devices with smaller channel length while the semiconducting behavior with larger channel length.

For doped nanonet devices, the high carrier concentration thus conductivity will not only come from the intrinsic properties of individual Sb-SnO₂ NWs, but also due to the modification of NW-NW junctions as illustrated previously. The generation of extra free electrons resulting from antimony doping will not only reduce the depletion layer of individual NWs according to the equation $W = L_d [\epsilon^2 \cdot N_{\text{SS}}^2 / 2 \epsilon \cdot N_D \cdot k \cdot T]^{1/2}$ while N_D is the donor state, but will also tend to reduce the energy barrier at the nano-junctions as suggested by the relationship $\Phi_b \propto 1/N_D$ (138). Since electron transferring through junction barriers is the dominant mechanism during transportation, diminishing of the energy barrier will result in significant increase of the amount of free carriers flowing within the nanonet.

Figure 4.24 The electrical performance of 0.5%Sb doped SnO₂ nanonets FET. (a) I_{DS} V_{GS} transfer curve, $V_{DS}=5V$; (b) I_{DS} V_{DS} output curve. $L=100\ \mu m$. All the testes were performed in air.

Thus, by controlling the dopant (antimony) concentration at around 0.5% (molar ratio, raw material), an air-stable semiconducting nanonet transistor was obtained. Figure 4.24 shows the electrical characteristic of 0.5%Sb doped SnO₂ nanonet FET. Unlike the pure SnO₂ nanonet introduced in the previous studies, 0.5% Sb doped SnO₂ nanonet devices can operate at a low voltage ($V_{GS}=5V$) while still maintaining a good saturation characteristics with $\mu_{eff}=2.86\ cm^2/V.s$ and $V_{th}=0\ V$. The dual sweeps show the air stable properties of the nanonet. The only drawback is the relatively larger hysteresis presenting in the transfer curves that are due to the mixed effect of O₂ and H₂O adsorption/desorption as previously discussed.

In short, tin oxide NWs with different antimony doping concentration were grown and their electrical properties were characterized in the format of large-scale nanonet field effect transistors. While XRD characterization showed the same curve regardless of antimony doping, both PL and XPS characterization indicated the existence of dopants. The I_{DS} V_{GS} transfer curves show the up-shift of OFF current with the increasing antimony concentration (raw material). This is due to the huge amount of electrons flowing in the nanonet which degrade the gate

voltage control. Air-stable, low-voltage driven device with $\mu_{\text{eff}}=2.86 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was obtained by controlling the dopant concentration at 0.5% molar ratio. This improvement is ascribed to the combined effect of increasing free carrier concentration and decreasing energy barrier at the nano-junctions.

c. Optical characterization of doped NWs via THz-TDS spectra

On the other hand, we found that the traditional investigation involving contact technique during the fabrication of FET would introduce extra influences which might confuse the characterization, such as the contact resistance and interface traps. Therefore, a complimentary and precise non-contact (optical) characterization approach is also introduced on SnO_2 NW based large area electronics investigation.

Terahertz time-domain spectroscopy (THz-TDS)(140) is emerging as an effective technique to investigate materials properties(141-144). THz-TDS is a spectroscopic technique in which the properties of objects are probed with short pulses of terahertz radiation. Because of the high signal-to-noise ratio, coherent phase detection as well as nonionizing and non-contact properties, THz-TDS has been demonstrated to be a highly sensitive and powerful technique to investigate the low frequency optical phonon modes and the high frequency free carrier behavior.

So in order to further characterize the properties of antimony doped tin oxide NWs, electrical parameters of these NW-networks were explored *via* a non-contact approach through analyzing of THz-TDS spectra, with the procedure and results shown below (more details in Appendix B).

The transmission terahertz spectra were carried out through a conventional THz-TDS system (TeraView Spectra 3000). Briefly, the 100 fs optical pulses centered at 800 nm with repetition

rate of 76 MHz from a mode-locked Ti:sapphire laser was focused onto a low-temperature-grown GaAs photoconductive dipole antenna to generate terahertz wave. The emitted terahertz wave was collimated and focused onto the sample through a pair of off-axis paraboloidal mirrors and then directed to a photoconductive detector. All the optical components and samples were enclosed in a chamber purged with dry nitrogen to minimize water vapor and oxygen adsorption. The transmitted THz pulse through the reference (empty substrate) and a representative sample were recorded in time-domain by altering the delay time between the THz pulse and gating optical pulse. Figure 4.25a displays the time-domain spectra of reference and a representative sample (0% Sb).

Figure 4.25 Measured time-domain THz pulses transmitted through reference and a representative sample. (b) Amplitude spectra in frequency-domain from Fourier transform of (a).

Compared to the reference signal, the main transmitted pulse peak intensity of the sample shows a significant decrease due to absorption. In each time-domain spectrum of Figure 4.25a, two transients were observed and the first one is the pristine pulse propagated directly through the media while the second transient is attributed to multiple reflections inside the media. The data analysis here was performed on the main transmitted pulse only without loss of validity. Figure 4.25b indicates the corresponding amplitude spectra in frequency domain after applying Fourier transform on the time-domain spectra in Figure 4.25a.

THz pulse passing through material is modified by the reflection and transmission at surface and interface, absorption of the material and dispersion in the material. The complex transmission coefficient can be obtained from the complex amplitude ratio of the transmitted THz pulses from the sample and reference. With the detailed calculation process in Appendix B, the measured frequency dependence complex conductivity of the three *n*-type nanonets with different free carrier concentrations were analyzed using Drude-Smith model. From calculation, it is obvious the dopant concentration increases, the mean free path of the free carriers decreases dramatically due to the increased structural defects and spatial constraints, with numbers are 1.64, 0.73 and 0.68 nm, respectively, which are much smaller than the average NW radius of ca. 60 nm.

Table 4.2. The carrier density, electron mobility and dc conductivity of three samples obtained by contact FET measurement and non-contact THz-TDS measurement.

Sample	$N_o (\times 10^{18} \text{ cm}^{-3})$		$\mu_m (\text{cm}^2/\text{V s})$		$\sigma_o (\Omega^{-1} \text{ m}^{-1})$	
	FET	TDS	FET	TDS	FET	TDS
0%Sb	0.6	4.05	11.5	77.62	567	1350
0.5%Sb	17.8	42.4	6.6	34.56	1911	2949
2%Sb	53.4	85.3	4.8	32.29	2612	3976

The effective electrical parameters of these three samples, free carriers concentration N_0 , obtained from the best fitting THz-TDS data, electron mobility, dc conductivity, were calculated and listed in Table 4.2. Mobility here is a phenomenological parameter inferring the carrier scattering rate which reveals the property of electrons population rather than an individual electron(145). In FET measurement, the electron states could be populated by free carriers substantially at equilibrium. The field-effect mobility is related to the statistical condition of the carrier momentum relaxation time τ at equilibrium(146). In the TDS measurement, the carriers studied are in non-equilibrium state, distributing to higher energy states than those at equilibrium or quasi-equilibrium. Their mobility would be determined by the scattering processes and energy relaxation at higher energies where the relaxation time τ is different(146).

As suggested in Table 4.2, the field-effect mobility is almost a fraction of the TDS mobility for each sample which is dissimilar from the results shown by Kozawa *et al.* in their Raman spectra and Hall measurement(147) as well as by Li *et al.* in their IR spectra study of GaN thin film(146). Unlike the Kozawa *et al.* paper, FET measurement here was based on tin oxide NW networks. As illustrated by the previous studies, the junctions between NWs will behave like energy barrier and localized/trapped states and free carriers will be severely reduced due to these existing states in the networks. In contrast, with regards to the TDS measurement, the effect of the barrier and trapped states will not be as prominent as horizontally aligned nanonet FETs, hence resulting in the carrier density difference. In short, the key difference between the two methods is that the FET measurement mainly concerns the NW-in-series which is inter-NWs property, while the TDS measurement focuses on the intra-NW property (electron oscillation within single-wires). However, both the FET and TDS methods revealed the clear trend of decreasing mobility with

the increasing in dopant concentration. This behavior is typically attributed to the coulomb scattering of charged impurity as well as the free carrier interactions(148). Compared with the values obtained through the contact measurement method, the dc conductivity of these three samples indicates higher values by calculation from the THz-TDS spectra. This is possibly attributed to the introduced contact resistance between the Al electrodes and the nanonets(149) as well as the extra energy barrier formed at the NW-NW junctions as discussed in the previous section. The Sb-doping would not only reduce the depletion layer of the NWs but also tend to reduce the junction barrier. Hence, with the increasing in dopant concentration, less distinction of the conductivity values are presented between the contact method and non-contact method as shown in Table 4.2.

4.2.3 Summary

Both water vapor and oxygen adsorption played important roles in the metal oxide FET system. In this study, SnO₂ NWs with varying O₂ concentrations in transporting gases, denoted as 0%O₂ and 0.5%O₂, were grown. HR-TEM and photoluminescence investigations identified the difference in these two samples in terms of surface-defect levels. An almost vanishing semiconducting behavior was shown when devices performed in humid air while the flow-in the dry air decreased the density of free carriers from almost conductive to 10¹² cm⁻², right-shifted the threshold voltage to -1.5 V and increased an ON/OFF ratio to 10⁶ for 0% O₂ sample. It was also observed that the process is reversible on the time scale of 100s. Under white light illumination, a significant photocurrent response was exhibited in the controlled environment for 0%O₂ nanonet devices while it is almost invariant for 0.5% O₂ devices. These results

confirmed the significant role of surface defects in metal-oxide NWs and these SnO₂ nanonet FETs bear a promising potential for the gas sensor and photodetector applications.

Impurity is another intrinsic factor that can affect the electrical properties of nanonets. Antimony doped SnO₂ NWs were obtained by using the SnO₂ and Sb₂O₅ mixture as the vapor source and the electrical parameters of SnO₂ nanonets were investigated with different Sb dopant concentrations through a contact approach (FET) and a non-contact optical approach (THz-TDS). These nanonet FET devices exhibit good device characteristics and the doping effects are well revealed by the device performance. Simultaneously, the same objective is achieved through analyzing the optical THz-TDS spectra using Drude-Smith model. To some extent, the THz-TDS spectra reveal more intrinsic physical parameters of the materials due to the absence of extra influence such as contact resistance introduced by electrodes deposition and junction barriers with localized/trapped states formed by electron transport from NW to NW.

4.3 Characterization of localized/trapped states existing at NW-junctions at low-temperature

In the previous sections, we have shown that highly oriented tin oxide (SnO_2) NW network based devices with excellent characteristics could be fabricated through contact printing. We have demonstrated that increasing the channel length resulted in degradation of the field-effect mobility. And it is clearly shown that there are lattice defects existing at the surface of NWs. Therefore it is reasonable to assume that charge transport in nanonet is limited by energy barriers at NW-NW junctions. However, efforts are still required to address questions like: how to quantify the energy barrier? Is anything present at the junction site? And how the electrons transfer over the barrier?

In this current study, we characterized the SnO_2 nanonet FET under controlled environment. In order to eliminate the other factors rather than NW-NW junction effect, devices with three different channel lengths ($L = 45, 100$ and $200\mu\text{m}$) were tested and compared. With this, the temperature dependent charge transport properties were clearly demonstrated in the large scale nanonet devices. The temperature effect on the hysteresis of the gate-regulated current curve, the threshold voltage, the charge mobility and the activation energy are reported and detailed discussed in this work. In addition, the band structure of tin oxide nanonet devices was also investigated.

The device fabrication and characterization follow the same way as introduced except liquid N_2 is used to bring the chamber (environment) temperature down to the required range (77K).

From the previous studies (33, 150), it is understood that for crystallized metal oxide single NW devices, they have temperature dependent field-effect mobility like the ZnO NWs discussed

below (Figure 4.26). The maximum mobility came from the lower electron-phonon scattering rate, caused by freezing out of phonons, and a lower electron-electron scattering caused by a decrease in the carrier concentration (from 300 °C decreasing)(150). This behavior is common in typical crystalline structures.

Figure 4.26 Temperature-dependent mobility (a) and carrier concentration (b) obtained for a 116 nm device, reproduced from [(150)]

4.3.1 Low-temperature effect on short channel devices

Figure 4.27 FET image with countable NW pieces and nano-junctions. (Red line indicate the NWs that bridging the source and drain while purple circle illustrate the junctions) Channel length $\rightarrow$ 20 μm ; No. of NWs connected the channel $\rightarrow$ 6; No. of nano-junctions $\rightarrow$ 10-15.

SnO_2 NW will be expected to have the similar behavior due to the single crystalline structure. We fabricated the following device (Figure 4.27) in order to examine both the NWs and nano-junction behavior under changing temperatures.

Since both single-NW and nano-junctions exist in the above-mentioned structure, device performance is expected to be the combination effect. The outcome of temperature dependent characterization is as shown in Figure 4.28. It is obvious that the field effect mobility and threshold voltage (carrier density) follows that similar trend as for crystalline single-NW devices. The interruption at around 200°C is believed to be the consequences of association of nano-junctions which will be touched in details in the following section.

Figure 4.28 (a) Transfer curves of the device at different temperatures; (b) output characteristics at 295K; Estimated temperature-dependent mobility (c) and threshold voltage (carrier concentration) (d) obtained from the device.

Even referring to the short channel length devices (15-45 μm , as shown in Appendix C), the single NW properties still dominate the device performance during low-temperature region as shown in Figure 4.29. The same figure also implies the nano-junctions may control the device performance at higher temperature after comparing the four devices beyond 220 K.

Figure 4.29 Temperature dependence of the NW conductivity, measured with $V_{GS} = 0$. with $\sigma = ne\mu$, n is the active carrier concentration. $K=A/L$, A and L are the cross section and channel length, respectively.

4.3.2 Longer channel length devices

Figure 4.30 (left part) shows the structure of nanonet FET device fabricated. Inspired by electron transportation in polycrystalline material (151), we assume the existence of localized/trapped states in the junctions as shown on the right section of Figure 4.30.

Figure 4.30 Illustration of the localized/trapped states existing at the nano-junctions.

Figure 4.31 The transfer curve and output characteristics of SnO₂ nanonet based TFTs. (a). Device was in vacuum under room temperature (300K). (b)-(d). The transfer curves of the devices tested under the temperature of (b) 77K, (c) 220K, and (d) 330K. Each step contains two consecutive dual sweep denoted as the 1st and 2nd run. The red arrows indicate the direction of voltage sweep. Insets of (b) and (d) show the output characteristics at the respective temperature step. Channel length $L=200\ \mu\text{m}$.

Figure 4.31a shows the typical transfer curve of the nanonet-based SnO₂ FETs at 300K. A mobility of 2.7 cm²V⁻¹s⁻¹ was extracted from the transfer curve for L=200 μm while μ = 5.6 cm²V⁻¹s⁻¹ was obtained for L=100 μm. The high mobility values are evidence that delocalized transport is present in this material. The mobility difference is mainly due to the increase number of nanojunctions associated with the larger channel length as previously discussed (134, 152).

As the NWs and junctions are connected in series, the effective mobility of the nanonet medium can be approximated as $1/\mu_{eff} = 1/\mu_w + 1/\mu_j$, where μ_w and μ_j are the mobility in the NW itself and in the junction barrier, respectively. As reported, electron mobility in single crystal can go up to 250 cm²V⁻¹s⁻¹(32), thus it is reasonable to assume that the overall mobility is dominated by charge transport limitations at the junction barriers.

Measurement of the temperature-dependent mobility was carried out in the vacuum chamber (~10⁻⁷ Torr) of a cryogenic probe station. Temperature was initially lowered down to 77 K followed by a steady increase to 350K. The transfer curve and output characteristics are shown in Figure 4.31b-d. It is obvious that with the increase of temperature from 77K to 350K, the hysteresis between the forward and backward sweep becomes more significant. Almost no hysteresis can be seen from the data obtained at 77K (until 160K), which indicates an electronically clean interface between SnO₂ NW, the Si₃N₄ dielectric layer and the surrounding environment; since oxygen adsorption/desorption is one of the main sources for the hysteresis, another possible reason would be that low temperature environment may not be able to provide enough thermal energy for the oxygen desorption process (since low temperature is helpful for adsorption). In the latter case, the minimum kinetic energy needed for desorption process can be calculated through the equation $KE_{avg} = 3/2 k \cdot T$ while $k=1.38 \times 10^{-23}$ J/K per molecule. Applied

to the current system, $KE_{avg} = 2.2 \times 10^{-21}$ J or 0.0137eV when $T=160$ K was adopted. It is also worth noting that when temperature increased beyond 220K (until 280K), the 2nd dual sweep of the $I_{DS}V_{GS}$ cycle will result in a right shift of the transfer curve, which may suggest the electron trapping between environment /NW/dielectric layer during that temperature stage.

By comparing the output characteristics ($I_{DS}V_{DS}$ plots) between 77K and 330K, the plots showed a slightly larger contact resistance at 77K while for 330K, the resistance is almost negligible. However, the effect for the contact resistance is insignificant during observation.

Figure 4.32 (a) The threshold voltage at different temperature; (b) $\ln(\text{mobility})$ as a function of $1/T$ at $V_{GS}-V_{TH}=20V$, as an example of the activation energy calculation; (c,d) mobility at different temperature as a function of $V_{GS}-V_{TH}$ which can be related to the sheet carrier concentration. (c) $200 \mu m$; (d) $100 \mu m$ (inset: $45 \mu m$ with short wires, which is different from previous one).

Since right shifts of the transfer curves were observed beyond 220K (until 280K) for 200 μm channel length and 200K beyond 100 μm , the relationship between threshold voltage and the temperature was plotted and shown in Figure 4.32a. In this study, both of the threshold voltage and electron mobility were calculated according to the method introduced in the previous work. It shows that for 200 μm , the V_{TH} initially decreases with increasing temperature which can be attributed to the fact that more carriers can escape from the localized states at higher temperature. This increase continued until 220K beyond which interface traps dominated by showing a sudden increase of threshold voltage (or decrease in carrier density). Same theory can be applied to devices with 100 and 45 μm channel length; however, it may not be that sensitive due to the relatively smaller active area and number of junctions.

The difference between instant gate voltage applied and the threshold voltage ($V_{GS}-V_{TH}$) can be related to sheet carrier concentration by the equation: $n_s = (1/q) C_{OX} (V_{GS}-V_{TH})$, where C_{OX} is the capacitance of the gate dielectric. V_{DS} is kept at a higher value than the $V_{GS}-V_{TH}$ for all the transfer curve measurements in order to ensure the mobility calculated is in the saturation regime. By fixing value $V_{GS}-V_{TH}$, the relationship of carrier mobility (μ_{eff}) as a function of temperature can be plotted, as shown in Figure 4.32b ($V_{GS}-V_{TH}=16\text{V}$). It shows that devices are thermally activated before critical temperature stage was reached which implies the existence of localized states (before 240K for $L=200 \mu\text{m}$ and 220K for $L=100 \mu\text{m}$). For thermal activation model, the effective mobility μ_{eff} is related to the mobility μ_0 in the transport band by an equation $\mu_{eff} = \mu_0 e^{(-E_a / kT)}$, where E_a is the activation energy and T is the temperature in K. By plotting $\ln(\mu_{eff})$ as a function of $1/T$, activation energy can be calculated by the equation:

$E_a = -(\text{slope of the gradient line}) \times k$, where $k = 8.617 \times 10^{-2} \text{ meV K}^{-1}$

For $L=200\mu\text{m}$, slope ~ -89.85 as from Figure 4.32b, $E_{a200} = 7.74\text{meV}$;

For $L=100\mu\text{m}$, slope ~ -37.35 as from Figure 4.32b inset, $E_{a100} = 3.22 \text{ meV}$;

Comparing the activation energy for various channel lengths, we can deduce that the NW-NW junctions played a significant role in the electron conductive process since E_{a200} is more than twice of the E_{a100} ,

In order to look through the problem in more detail, Figure 4.32c&d (including inset) exhibit the saturation mobility at different temperature ranging from 77K to 330K as a function of $V_{GS}-V_{TH}$ (or carrier concentration) for the three different channel lengths. For channel length $200\mu\text{m}$, the transport seems to be thermally activated regardless of the sheet carrier density for temperature below 180K, this is evident from the nearly linear as well as parallel lines exhibited in Figure 4.32c. This phenomena of thermally activated mobility can be applied up to 240K when $V_{GS}-V_{TH} < 7\text{V}$. However, there are obvious saturations when temperature goes beyond 220K which indicates the limitation by surface/phonon scattering (153).

Comparing Figure 4.32d (including the inset) with Figure 4.32c, it can be seen that with the decrease of the channel length, the surface/phonon scattering effect become less dominant as evident from disappearance of the saturation curve above 200K. For channel length of $45 \mu\text{m}$, the temperature lines even crossed over at $V_{GS}-V_{TH} \sim 13\text{V}$ which means decreased electron mobility with the increasing temperature. This may suggest a band-like transport beyond that stage. As claimed by Lee et al (154), the crossover from the thermally activated to band-like

transport is only observed in the sample with high carrier concentrations which is compliant with the electrical characteristics of the short channel length devices.

Figure 4.33 (a)(c) Mobilities at different $V_{GS} - V_{TH}$ as a function of $1/T$; (total 10 data point were taken for each curve in a, and 8 points for c); (b)(d) Activation energy as a function of sheet carrier concentration. Insets are examples to calculate the active energy, different linear gradient at different $V_{GS} - V_{TH}$ can be seen from the figures. [(a)(b), $L = 200 \mu\text{m}$; (c)(d), $L = 45 \mu\text{m}$].

Since $V_{GS} - V_{TH}$ can be related to the sheet carrier concentration, all the four graphs in Figure 4.33 presented the relationship of either electron mobility or activation energy with varied carrier concentrations. Figure 4.33a&c shows the mobilities at different $V_{GS} - V_{TH}$ as a function of $1/T$. It is obvious that for $L = 200 \mu\text{m}$, with the increasing of temperature, all the concentration curves are experiencing a significant drop of the mobility as shown in Figure 4.33a. This is consistent

with the right-shift of the threshold voltage. It is also noted that lower electron carrier concentration will be more readily trapped than higher concentration as evident from the earlier and more severe dropping of the mobility curve. The effect is more prominent for samples with lower carrier concentration since a significant proportion of electrons are trapped in this process.

Figure 4.33b shows the activation energy (E_g) as a function of sheet carrier concentration (n_s). Six temperature points ranging from 100 K to 220 K were employed to the linear fit (Figure 4.33b, inset). This is to avoid the disturbance of the mobility beyond 220K as illustrated in Figure 4.33a. The coefficient of determination r^2 for all the fitting lines are all larger than 0.95 with the standard error of the slope calculation being less than 10%, which means the experiment data fits very well to the multiple trap and release (MTR) model. The figure shows a clear trend that with the increase of the sheet carrier density, the activation energy is gradually reduced from 16.24 meV ($V_{GS}-V_{TH}=0.5V$) to 6.50 meV ($V_{GS}-V_{TH}=18V$). Based on previous studies(155), the decreasing trend of E_a indicates that as the gate voltage increases, more electron carriers tend to fill up the localized/ trapped states at the junction site, hence the energy distance between the filled trap states and the transport states reduces.

Transport in different regimes exhibits different dependence on temperature for $L=45\mu m$. This can also be seen from Figure 4.33c & d. The activation energy decreases with increasing carrier concentration until mobility edge is reached at $V_{GS} - V_{TH} = 13V$. In this regime, transport is thermally activated and dominated by MTR model. Beyond the mobility edge, the localized/trapped states were fully filled up and the charge is transporting in the delocalized states. In this regime, the effective mobility reduces with increasing temperature due to surface/phonon scattering and band transport is the dominant transport mechanism.

Figure 4.34 (a) A cross point can be obtained by extending the temperature curves in (c); (b) linear line was fitted in the activation energy verses carrier concentration graph. (c) Simplified band energy diagram of nanonet with respect to the density of states for 45, 100 and 200 μm channel length devices.

Following the same concept, the mobility edge for larger channel lengths of 100 and 200 μm can be calculated and predicted as shown in Figure 4.34. By extending the temperature curves of Mobility vs. $V_{GS} - V_{TH}$ (Figure 4.32c), a cross-point was obtained beyond which the higher temperature will result in a lower mobility. This point can also be calculated by locating the sheet carrier concentration at zero activation energy. For both of the methods, a critical point of $V_{GS} - V_{TH} = 32$ V will be achieved for $L=200\mu\text{m}$ and $V_{GS} - V_{TH} = 28$ V for $L=100\mu\text{m}$.

Therefore, we are able to draw the relationship between band energy and density of states as in Figure 4.34c and conclude that the localized/trapped states do exist at the NW-NW junctions.

With the increase of channel length (number of nano-junctions), more localized/trapped states are present hence more carriers are needed to fill up the states before band-like transportation is shown.

Figure 4.35 Temperature dependent conductivity of Sb doped SnO_2 nanonet devices. The inset shows the I-V curves of device fabricated at different points.

Temperature dependent conductivity of Sb doped SnO_2 NWs were obtained which also shows the platform around 220K is caused by the possible activation of traps at wire junctions (Figure 4.35), which further confirms the authenticity of our previous assumption.

4.3.3 Summary

In conclusion, SnO_2 nanonet FET were characterized under controlled environment with the temperature varying from 77-350K. Devices with three different channel lengths (45, 100 and 200 μm) were tested and compared. The relatively larger hysteresis can be attributed to the activation of O_2 beyond certain temperatures hence the energy for the O_2 adsorption and

desorption was calculated to be 0.0137eV. For devices with larger channel length, an obvious drop of mobility and right-shift of the threshold voltage was observed beyond 200K attributing to the trapping and de-trapping of the electrons at the interface of NW and dielectric. Before the critical temperature at which trap at interface of dielectric and NW happens, nanonet devices are thermally activated and the activation energy is calculated to be higher for devices with bigger channel length. For the device with smaller channel length, a clear mobility edge was observed at $V_{GS} - V_{TH} = 13$ V beyond which mobility will decrease with the increasing temperature. This threshold carrier density tends to exhibit an escalation with an increase of channel lengths which implies the existing significant amount of localized/trapped states at the nanojunction sites.

4.4 Interactions of oxide NWs with organic and inorganic materials and DSSC integration

4.4.1 Interaction with organic polymers

Organic semiconductors have attracted much interest in large-area and flexible electronics by their solution processability and reasonable semiconducting properties. However, the relatively low field-effect mobility and stability of organic TFTs may limit their widespread adoption as discussed before. The use of NW networks in conjunction with organic semiconductors is also a feasible approach to fabricating large scale printed devices with unique properties. It has been reported that combination of ZnO NW network and n-type semiconductor Phenyl-C61-butyric acid methyl ester (PCBM) exhibited enhanced n-type behavior compared with pure PCBM TFT, as shown in Figure 4.36(156). The saturation field effect mobility is reported to be 0.561 cm²/Vs for the hybrid structure which is 17 times over the pristine polymer (0.034 cm²/Vs). This is attributed to the superior semiconducting properties of ZnO single crystalline NWs. The NWs acted as conducting bridges between crystals in PCBM which not only enhance electron transport but also increase the number of charge carriers in the transport channel.

Figure 4.36 Transfer characteristics of ZnO NW-PCBM composite transistors with the device structure as illustrated in the right corner. (reproduced from (156))

In other several studies, the same concept has been exploited, for instance, the incorporation of CNTs in the fabrication of solution-processed p-type composite TFTs. These nanotubes were introduced into regioregular poly(3-hexylthiophene) (*P3HT*) and PQT-12, both of which are p-type organic semiconducting polymers. However, there are few reports concerning solution-processed p-type OTFTs combined with n-type metal oxide NWs. Here, we introduced two approaches that polymer semiconductor can be incorporated with the inorganic NW networks. First format will be the non-continuous photosensitive polymer on top of nanonets followed by continuous layer of polymer on top of nanonets. The polymer used is commercial *P3HT*.

Figure 4.37 Transfer curve (a) and photo-response (b) of pure P3HT (10mg/ml after annealing)

As shown in Figure 4.37, pure P3HT shows typical p-type behavior with carrier mobility around $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ and good light sensitivity.

a. Non continuous P3HT coating formed by spinning coating 1mg/ml P3HT in chloroform solution following by chloroform rinsing.

In absolute terms, for a given number of photons per unit area, the photo-induced changes in pristine NW FETs are relatively small compared to semiconducting polymer based FETs which offer a large area of absorption cross section for photo-carrier generation and transport (Figure 4.37 and Figure 4.19). However, in terms of dark-transfer characteristics, NW based FET is significantly better compared with polymer based ones. A combination of the characteristics of the two classes of FETs in a single device offers interesting possibilities.

Such combination can offer the existing NW FET with increased carrier density, hence effectively modification of the threshold and driving voltage.

Here we present the studies of regioregular poly(3-hexylthiophene) (P3HT) non-continuously dispersed on SnO₂ nanonet structures which reveal the interesting features resulted from combination of molecular process initiated by photo-excitation of polymer and transferred to the nanonet, with the results shown below.

Figure 4.38 (a)(b) Transfer curves and output characteristics of P3HT particles on SnO₂ nanonet devices; (c) photo-sensing behavior of the hybrid structure under light pulse conditions at very low frequency (0.05Hz) with the mechanism illustrated in (d).

In this particular study, nanonet structures with relatively (intermediate) low level of concentration of polymer matrix were used. Regioregular P3HT (Sigma Aldrich) in chloroform solution (1mg/ml) was spin coated on the nanonet device substrate following by thermal annealing at 140°C for 30 mins in nitrogen environment. A quick chloroform rising was

performed after the annealing which significantly reduced the chance of polymer chains to form a continuous coverage between the electrodes.

The electrical characteristics of the device in dark do not indicate any noticeable alteration upon addition of the polymer. The magnitude of saturation current and output curves remain almost the same. However, the transfer characteristics are drastically altered upon photoexcitation with a significant increase of the OFF current and right-shift of the threshold voltage (Figure 4.38a). The $I_{DS}V_{DS}$ characteristics tend to be linear almost regardless of the applied gate voltage (Figure 4.38b).

It is worth noticing that in the device structure without nanonets, the same level of polymer content (after chloroform rising) did not demonstrate FET characteristics due to the discontinuity of the layer. Hence all the behavior discussed here are with the polymer-NW interfaces where the photo-generated charge carrier transfer from P3HT to tin oxide NW networks. Theoretically, upon illumination, the excitons (electron-hole pairs) are generated within P3HT domain and dissociated at the place where electrical potential exists, and for most of the cases, it is at the interface of p-type and n-type material. This process could be more effective in the depletion mode where the induced positive charge on the surface of the NW provides a sink for the photo-generated electrons(157).

With regards to the dynamic current study (Figure 4.38c), the large ON/OFF ratio in the polymer/nanonet composites favors a potential application for photo-detection. However, persistence of the current was observed after it switched off. This could be due to the charging of the defect sites at polymer/NW interface, resulting in a formation of charged dielectric layer

at the interface over a time period and effectively inducing the high I_{DS} after switching off the light.

b. Ambipolar transistor based on SnO₂ nanonet/P3HT (10mg/ml in chloroform, spin-coat)

Figure 4.39 Transfer characteristics of an SnO₂ NW network-P3HT composite layer displaying ambipolar characteristics.

The combination of a continuous layer of p-type organic semiconductor and an n-type metal oxide NW network allows ambipolar operation of the transistor. Figure 4.39a&b displays the electrical characteristics of such a transistor. Spin-coating a layer of P3HT (10mg/ml in chloroform) over SnO₂ transistor allows the operation of the transistor in two regimes. In the testing configuration displayed in Figure 4.39b inset, the drain and the gate terminals of the transistor are grounded and only the source voltage is modulated. The application of a positive source voltage induces negative gate, drain bias and thus accumulates holes in the transistor channel. Conversely, the application of a negative source voltage induces electrons in the transistor channel. Since the mobility of organic semiconductors are generally lower than that of the SnO₂ nanonet devices, the current levels in the two operating regimes are asymmetric. The

output characteristics also diverge noticeably as shown in Figure 4.40. Further optimization of this category of metal oxide-organic semiconductor nano-composite transistors would involve the morphology control of the organic semiconducting layer to improve performance, as well as the deposition of an interlayer between the n-type semiconductor and p-type semiconductor to prevent recombination of the charge carriers.

Figure 4.40 Transfer curves and output characteristics of the ambipolar devices.

4.4.2 Interaction with inorganic p-type material

Besides polymer used for organic solar cells, NWs can also be integrated with other photosensitive materials like p-type copper indium gallium selenide (CIGS) to explore the application of NWs in thin film photovoltaics. In the current study(158), we investigated the

potentiality of CIS/SnO₂ type device for photovoltaic generation. CuInSe₂/SnO₂ core-shell and hierarchical branched nanostructures were produced by directed electrochemical assembly (DECA).

Figure 4.41 On the top: illustration of deposition setup; Bottom: FE-SEM images of CIS/SnO₂ in different growth zones from anode to cathode: (a) region 1: dot formation; (b) region 3: 80% coverage; (c) region 5: 100% coverage; (d) region 6: branched structure. (158)

The morphology and stoichiometry of deposited product can be controlled by changing the spatial electric field along the deposition region, and core-shell structures from In-poor-CuInSe₂

nanoparticles/NW to near stoichiometry CuInSe_2 branched NWs can be formed as shown in Figure 4.41a-d. Combined characteristics of FESEM, TEM, XRD and Raman spectroscopy reveal that both morphology and chemical compositions of CuInSe_2 strongly depend on the spatial electric field distribution on the SnO_2/Si substrate(158).

Figure 4.42 Dynamic study under pulse light conditions of very low frequency of the photocurrent generation for CIS films deposited at different positions at -0.4V vs. Ag/AgCl in 0.1M KPi pH7 buffer electrolyte.(158)

In order to identify the relationship of morphology and chemical composition of deposited nanostructures with the photon-to-electron conversion properties, the photocurrent response was investigated through photoelectrochemical study(159). Figure 4.42 shows transition photocurrent of CIS/SnO_2 at applied potential -0.4V vs. Ag/AgCl , using 0.1M KPi pH7 buffer electrolyte solution and under white light illumination. All deposits are p-type semiconductors with cathodic photocurrent(159). In-poor-CIS film obtained in the region 1 showed lower photocurrent (anode, $15\mu\text{A}\cdot\text{cm}^{-2}$) than In-rich-CIS films obtained in the region 3(middle,

$30 \mu\text{A} \cdot \text{cm}^{-2}$) and region5 (cathode, $35 \mu\text{A} \cdot \text{cm}^{-2}$). It suggests that In-poor-CIS has much weaker photochemical response compared to CuInSe_2 .

4.4.3 DSSC application

The optoelectronic properties of metal oxide NWs promises great potential applications in dye sensitized solar cells (DSSCs)(160-161). The use of NWs in the cell structure allows the formation of a direct conduction path for the photogenerated carriers to the electrode in contrast to the 0D structure based solar cells where the conduction is slowed by charge hopping events between individual particles. This ensures much higher carrier mobility in the NW based solar cells than the nanoparticle ones.

At the same time, electron separation and transfer as the most basic process in photovoltaics are also drawing researchers' attention. In these cells, the interfacial electron transfer process is governing the efficiency of light to current conversion in the devices. Most of the established interfacial electron transfer studies are focused on conventional TiO_2 nanoparticles, however, there is a limited report on the transfer study with SnO_2 , esp. in the format of NWs.

Continued from the previous study (aligned tin oxide nanonet), we reported the photoexcitation effect of N719 dye on tin oxide NWs in this section. The current enhancement upon photo illumination was investigated in different gas environment. Ultrafast study of electron injection on Ru-dye sensitized tin oxide nanonet was also conducted. For the first time, the nanonet structure was integrated in to solid state DSSCs with spin-coated hole conducting layer.

Figure 4.43 $I_{DS}V_{GS}$ transfer curves of nanonet devices in different gas environment w/o (a) and w/ (b) N719 dye coatings (output characteristics is shown in Appendix D).

As reported in the previous section, SnO_2 nanonet-FET shows various electrical characteristics in different testing environment due to the large surface area and modification of the energy barrier at nano-junctions. When the devices were exposed to open air with 50% humidity, both the ON and OFF current increased dramatically as shown in Figure 4.43a. The significant increase of free electrons weakened the gate modulation effect and the transistor characteristics became less prominent. The purging of Dry Air (mixture of $\text{N}_2 + \text{O}_2$, H_2O concentration < 100ppm) would recover the semiconducting behavior. The right-shift of the threshold voltage and enlarge of the hysteresis are due to the oxygen adsorption/desorption as mentioned before.

The same FET devices were then immersed in N719 dye solution (acetonitrile as solvent) for 24 hours to allow the dye adsorption. It is known that N719 dye which contains two carboxylic groups has also been ascertained to bind via two carboxylates, as shown in Figure 4.44, which promote electron transfer upon photoexcitation (162). The attachment of N719 dye on the NW surface enhanced the sensitivity of the nanonet FET to the surrounding environment as shown in Figure 4.43b. While the electrical performance in vacuum is nearly the same before and after

the dye attachment, the exposure of air degraded the semiconducting characteristics severely. Dry air purging shifted the threshold voltage much further to the right and OFF current decreased by one order in the same time with enlarged hysteresis. To confirm the oxygen effect, pure Ar gas (99.99%) was pumped-in and the transfer curve tended to shift back to the initial position. The existence of a trace amount to oxygen and water molecules in the testing chamber retarded the restoration.

Figure 4.44 Schematic energy diagram of and photoinduced charge separation process in N719 dye / tin oxide nanomaterials.

Figure 4.45 (a) $I_{DS}V_{GS}$ transfer curve for tin oxide nanonet device with N719 dye attachment (w/ and w/o light illumination); (b) Dynamic light response dye coated nanonet device when $V_{GS} = -20$ V (location a); (c)(d) Dynamic light response of nanonet device w/ and w/o dye attachment when $V_{GS} = 20$ V, different gas environment were adopted during testing.

Upon illumination (Halogen light source with the intensity of $2\text{mW}/\text{cm}^2$), electron injection from the dye introduces current enhancement in the tin oxide nanonet FET (Figure 4.45). It alters the energetic of the quasi-Fermi level of tin oxide and creates a potential gradient within the cross-section of NWs, which forms the driving force for electron transport. Figure 4.45a showed the photocurrent change on SnO_2 nanonet FET before and after the dye attachment. Devices were tested in vacuum ($\times 10^{-5}$ Torr). Compared with the almost negligible enhancement of bare tin oxide nanonets, the OFF current for dye attached devices increased by 10^4 times under light illumination which made it a promising photodetector as shown in Figure 4.45b. The dynamic light response when devices w/ and w/o dye coating is shown in Figure 4.45c & d for

devices tested in vacuum, open air and dry air, with both V_{GS} and V_{DS} equal to 20 V (location b in Figure 4.45a). The decrease of light current when devices in air and dry air is suspected to be mainly due to the oxygen or/and water vapor attachment on dye.

Figure 4.46 Illustration of the pump-probing technique.

Pump-probing (two-color femtosecond transient absorption spectroscopy) technique was adopted to characterize the photoinduced interfacial electron transfer (ET) dynamics from dye to tin oxide NW upon illumination (144, 163). The basic mechanism of pump-probing is as shown in Figure 4.46. Generally, transient absorption spectroscopy use two pulses (strong pump with shorter wavelength and weak probe with longer wavelength) and is capable of achieving a high temporal resolution. A sample is excited by the pump pulse which triggers the process under investigation following by a second delayed pulse, the probe, which monitors the optical properties including (reflectivity, absorption, luminescence, Raman scattering) during the process. Hence the measurements as a function of time may be assembled by varying the time delay between the pump and probe pulses. Figure 4.47 shows the ultrafast transmittance profile of

N719-SnO₂ system on two different time scales (0-500 ps and 0-3ps). These transient absorption (or transmittance) data were obtained with a pump at 530 nm and probe at 770 nm. Electron injection into semiconductor conduction band is activated upon photoexcitation of the attached dye molecule. Both the SnO₂ conduction band electrons and the dye oxidized states have contributions to the transient absorption in this spectral region(164). It is worth noting that the N719 excited state could also absorb in this region (red to near-IR), but the signal detected is thought to be mostly due to the oxidized dye since the rise time is not instrument response limited (200 fs) but much slower(163).

Figure 4.47 Normalized transient IR kinetic traces for pure dye film (purple squares) and dye+SnO₂ nanonet film (orange pentagons) and their multiexponential fit (solid line). Inset is the zoom in of dye+SnO₂ which shows the rise time of 470fs.

Based on energetic structure, SnO₂ is expected to provide better electron injection rate compared to TiO₂ since its E_{CB} edge position is 0.5 eV lower than that of TiO₂. However, the rate of electron injection (~ 470 fs) is characterized to be slower than TiO₂ (< 100 fs)(165-166). It may be due to the presence of dye agglomerates on the metal-oxide NWs caused by different amounts

of dye loading, resulting in slow charge injection (167). Another possible scenario is that the rate of electron injection under nonadiabatic condition is proportional to the available density of accepting states (DOS) in the conduction band of semiconductor (167). The higher DOS in TiO_2 by almost 2 orders facilitate the faster electron injection into TiO_2 than SnO_2 (168).

a. Horizontal charge collectors

The characterizations above confirmed the feasibility of integrating the highly conductive and transparent tin oxide nanonet into solar cells as photoanode. The fabrication of solid state DSC was completed by spin-coated $2\mu\text{m}$ spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene) as the hole conducting layer, with structure as shown in Figure 4.48 insets. Direct electron transfer path is provided by metal oxide NW's network in this case.

Figure 4.48 I-V characteristics of the solar cells made from SnO_2 NWs w/ and w/o antimony doping. Illustration of the cell structure is shown as inset. Aluminium electrode here is comb shape so dye sensitized tin oxide NW can directly contact with the hole conducting layer. (134)

Figure 4.48 shows the cell performance under the standard $100\text{mW}/\text{cm}^2$ power AM 1.5 filtered Xenon light source (SAN-EI ELECTRIC XES-301S solar simulator) and IV was recorded on Agilent semiconductor parameter analyzer 4155C. Higher photovoltages are observed with the NW-solar cell system compared with tin oxide nanoparticles ($\sim 300\text{ mV}$), this has been attributed to the slower recombination kinetics and lower work function of SnO_2 NWs compared to the nanoparticles(169). Besides the higher V_{oc} , the solid-state DSC incorporating pure SnO_2 can barely be considered a solar cell since the photocurrent at short-circuit is almost negligible (0.04 mA cm^{-2}), leading to a power conversion efficiency of less than 0.01%. The lower current can be attributed to the following aspects: 1).The primary limitation will be the reduced amount of dye loading since the thickness of the single layer nanonet is only $100\sim 200\text{nm}$. It has been reported that if on the basis of same film thickness, the loading of dye can be much higher in 1D nanostructured material than the nanoparticles (170). The thickness of nanoet can be increased by repeated transferring (still not practical to reach $4\sim 6\text{ }\mu\text{m}$). 2). The second disadvantage comes from the trap interface between two adjacent NWs as we always emphasized. NW-NW junctions in n-type metal oxide nanonets are considered as defects due to the existence of energy barrier and localized/trapped states. Electrons tend to be trapped in the localized/trapped states, leaving a net negative charge at the junctions which sequentially attracts minority carriers into the junction area, resulting in an increased probabilities of electron-hole recombination in this region.

Conductivity of nanonet can be improved by antimony doping as introduced. As previously characterized, Sb^{5+} will substitute Sn^{4+} in the compound and contribute one extra free electron, thus, adding specific amount of antimony will be able to moderate the electrical behaviors of

SnO₂ nanonet from semiconducting to metallic-conducting behaviour. The increased electron carrier density will also reduce the thickness of surface depletion layer hence diminish the trapped/localized states. The red curve in Figure 4.48 shows the improvement of the current density by adopting 5% Sb/SnO₂ nanonet (molar ratio in raw material) and current increased by 4 times with the same thickness of nanonet layer.

b. Vertical tin oxide nanonet as charge collector

The above mentioned horizontal collection study demonstrates a feasible way for the NW to be applied in solar cells. However, the relatively low efficiency retarded the further study of the NW parameter such as diameter and length-effect since the difference was hard to distinguish. In this case, we applied the as-synthesized vertical NW network structure directly into dye-sensitized solar cell. Since silicon substrate is used in the VLS growth process (high temperature), back-illumination DSSC structure has to be adopted due to the opaqueness of silicon substrate. The effect of NW physical properties such as length and diameter on the performance of liquid DSSC performance was studied here. The adjustment of the NW length was realized through control of growth time while the diameter was controlled by modifying the thickness and annealing condition of catalyst layer. A good understanding of applying tin oxide nanonet structure in DSSC is expected to be achieved in the end.

Vapor-Liquid-Solid (VLS) process is used in order to get highly crystalline SnO₂ NWs. Besides, better control of NW parameters was also achieved with ease in this way. The initiation of anisotropic crystal growth using metal nanoparticles as catalysts provided a practical way to alter the NW diameter by controlling the initial metal nanoparticle size. And the length of NWs can be modified by changing the growth duration. After being scratched into a 5mm circular region

(to control the active area), the substrates were immersed into N719 dye solution for 24 hours for dye molecules to be attached onto the NW surface. Counter electrodes made from Pt solution were also prepared at the same time on FTO glass. The structure and components of the fabricated solar cell is schematically shown in Figure 4.51. Electrolyte R50 (Iodolyte R50, Solaronix SA, Iodide based redox electrolyte) was injected into the cell by vacuum pumping method followed by the hole sealing.

Efficiency testing was done under the standard 100mWcm^{-2} power AM 1.5 filtered Xenon light source (SAN-EI ELECTRIC XES-301S solar simulator) and IV was recorded on Agilent semiconductor parameter analyzer 4155C.

To study the effect of physical properties of NW on the performance of solar cells, several parameters were modified and investigated including the length and diameter. The main disadvantage of using Si substrate is its opaqueness, which blocks the incident light from transmitting through the cell from the substrate side. A back-illuminated structure has to be used for the cell fabrication. However, transmission through all these layers (FTO glass + Pt coating + electrolyte) may reduce greatly the amount of light that can reach and be absorbed by dye, which will directly affect the current density and ultimate efficiency of the solar cell.

Another issue is with the semiconductor nature of silicon substrate. Compared to the traditional conductive FTO glass substrate, semiconducting silicon substrate used here has disadvantage in the electron collection, due to its band-gap and lower Fermi-level. Nevertheless, the main purpose of this study is to investigate the effect of the physical properties of NWs on performance of solar cells and the side effect of Si substrate can be minimized through comparison and normalization. It is worth noticing that a compact layer of SnO_2 formed

between the NW network and the Si substrate during the VLS growth (Figure 4.49), which may perform as the hole blocking layer during device performing.

The effect of NW length

Figure 4.49 Cross-section view of the as-grown NWs (NW grown for 40mins, inset shows the NW after top-pressing). (171)

The length of the tin oxide NWs was firstly considered and tested. Since shorter NW implies shorter travelling path, it's more probable that electrons are able to transfer through the path and get collected at the substrate. However, it may also lead to smaller surface area for dye attachment. On the other hand, longer NWs contribute to more dye loading and charge generation, but less effective charge collection at the substrate due to longer channels than the normal electron diffusion length.

As we can see from Figure 4.49, the NWs were not vertically aligned on the silicon surface due to the lattice mismatch between SnO_2 and the Si substrate, which makes it difficult to measure the exact length of the NW. Film thickness was adopted here to represent the NW length. On top of this, the ultra-long NWs that pop out may cause short-circuit during cell fabrication. Pressing the as-grown NWs gently by placing 1cm x 1cm Si wafer (+ fixed weight) on top can solve this problem as shown in Figure 4.49 inset. It should be noted that the actual NW length can be much larger than the film thickness (after top-pressing), and longer NWs or thicker films were obtained as growth time prolonged (Figure 4.50).

Figure 4.50. Thicknesses of NW films grown on 2nm Au layer on Si substrate (after top-press)

The solar cell parameters produced from the devices with different NW thicknesses are summarized with the typical IV curve of the solar cell as depicted in Figure 4.51b. As described, longer wires provide more anchor points for dye molecules which will increase the number of free electrons generated during light illumination; hence the current density and efficiency value start to increase along with the increase of NW growth time, which is shown in Figure 4.51c&d. As the wire length reaches a certain value, with film thickness of around 40 μm , the electron

collection efficiency at the substrate side starts to decrease as the wires are too long for the electrons to diffuse through, which leads to lower current density hence cell efficiency. In addition, capillary effect may also make it more difficult for dye solution to penetrate into the longer and denser NW network structure, which may result in the reduction of dye loading capability.

Figure 4.51 Plots of (a) illustrated structure of NW solar cell; (b) typical IV curve; (c) – (f) efficiency, J_{sc} , V_{oc} and Fill Factor of NW films with different thicknesses, all NWs were grown on 2nm Au catalyst layer.(171)

The open circuit voltage (V_{oc}) of the fabricated cells remains around 0.25V in the beginning (Figure 4.51e). This value is lower than the theoretical value which is the offset between the conduction band and the redox potential (0.5V). This may be attributed to heterojunction formation at the Si-SnO₂ interface and the recombination reactions inside the cells. The fill factor remains at around 0.33 (Figure 4.51f), which is much low compared to TiO₂ nanoparticle based cells (0.6-0.7). As known, fill factor is a measure of the squareness of the I-V curve, which can be affected by the series resistance and shunt resistance of the cell. An increasing series resistance will reduce the slope of the I-V curve at open circuit point and an increasing shunt resistance will reduce the slope at short circuit point accordingly. With the use of the Si substrate, which has lower current collection efficiency due to its semi-conductivity, the series resistance at the interfaces will be very high, resulting in the decrease of current output.

The effect of NW width.

Tin oxide NW is the transport channel for free electrons and the mobility of electron inside the NWs can be affected by the width of the NW as illustrated in Figure 4.52, hence the diameter of NWs can further influence the cell efficiency.

Figure 4.52 NWs with smaller diameter will exhibit a relatively thicker depletion layer compared to the size, which will result in a narrower conductive channel.(171)

Figure 4.53 SEM pictures of a) Indication of the Au particle on the tip of the as-grown NW; Au nanoparticles and the corresponding NW from b)&c) 2nm Au layer, d)&e) 10nm Au layer. (171)

Referring to the VLS growth mechanism, the diameter of NWs is decided by the size of Au nanoparticles or the thickness of Au layer. Hence, Au layers with different thicknesses ranging from 2nm to 10nm were deposited on Si substrate by electron-beam deposition. Thicker Au layer would be expected to produce larger Au particles when melted which results in larger final diameter of the NW grown.

The melted gold nanoparticles with different sizes and the corresponding NWs grown are shown in Figure 4.53. The diameter of Au nanoparticles produced from the 2nm Au catalyst

layer is in 32.8-38.7nm range which resulted in the smaller NW diameter (70-80nm). On the other hand, 10nm thick Au catalyst will finally grown into NWs with 110-120 nm diameter.

Figure 4.54 Plots of a)efficiency, b) J_{sc} for cells fabricated from NWs grown from Au layers with thickness of 2nm, 6nm,10nm.(171)

From Figure 4.53a, it should be noted that cells made from thicker NWs (10nm Au) have better efficiency than those from thinner wires(6nm, 2nm Au). With larger diameter of the NWs, the electron conduction channel will become bigger and less scattering along the wire is expected during the charge transport as compared to narrower NWs (152). It helps to increase the electron transport in the semiconductor material by showing higher J_{sc} as in Figure 4.54b, hence the cell efficiency. For each different Au layer, the efficiency value will also be optimized at certain NW thickness, which is consistent with the previous study of the length effect.

4.4.4 Summary

In terms of photo-excitation, the hybrid structures of NW with both organic and/or inorganic p-type photo-sensitive materials were examined. Coating of a discontinuous (diluted) layer of P3HT will enhance the photocurrent effect by transferring the generated electrons to the nanonet, making the device function as photodetector; at the same time, a thicker layer of P3HT allows ambipolar transistor behavior. The deposition of CIS on SnO_2 through DECA was also demonstrated. Controlling over the morphology and chemical composition of CIS deposited generates different functionality as observed from the photocurrent measurement. These nanostructures are believed to have immense potential for solar energy harvesting.

Photocurrent response of N719 dye coated tin oxide nanonet FETs were characterized under different gas environment. The adsorption of water vapour and oxygen molecules on to dye- SnO_2 system severely degraded the transistor behavior. OFF current was significantly increased upon light illumination due to the significant amount of electrons generated and transferred from the Ru dye. A rise time of 470 fs was obtained through two-color femtosecond transient absorption spectroscopy. On top of the basic characterization, the potential application of horizontally aligned tin oxide nanonet in solid state DSC was also demonstrated.

Dye-sensitized solar cells were also fabricated from the vertically grown tin oxide NW film on silicon substrate followed by standard DSSC fabrication. Back-illumination structure was used due to the opaqueness of silicon substrate, which is a limiting factor for the highest cell efficiency achievable. The effect of physical properties of NW such as length and diameter on the cell efficiency was studied. NW film thickness of 40 μm after the growth for 60 mins generated the highest cell efficiency due to the balance between large surface area for dye

Chapter 4: Results and Discussion

attachment and the relatively short direct path for charge transport. NWs with larger diameter showed a remarkably increased current density which is due to the presence of less scattering centers along the transport path.

Chapter 5

SUMMARY and CONCLUSIONS

Crystalline inorganic semiconducting NWs have demonstrated excellent performance for electronics in a broad spectrum of research. Subsequent to the high temperature pre-processing of high crystallinity nanowire materials, device fabrication may be pursued at room temperatures; and thus is compatible with a wide range of substrates, including plastic and paper. Oxide NW with superior quality grown at high temperatures thus form a very attractive material sets with properties that can find applications in nanoelectronics and photovoltaic energy harvesting.

Highly crystallized SnO_2 NWs were grown in this study through CVD process and parallel-array SnO_2 nanonet field-effect transistors fabricated by direct-contact printing displayed the high charge carrier mobilities even at large scales. The surface state dependent electron mobility measurement under different environmental conditions indicated that the adsorption/desorption of oxygen molecules lead to a change of the depleting thickness on the surface of the NW hence energy barrier at the junctions, which affects the electron transport properties in these nanonets. Despite an inferior electrical performance at the NW junctions with low-density, the junctions helped to improve the semiconductor behaviour in high-conductive or high-density nanonet devices. Surface passivation with polystyrene and SiO_2 overlayers has stabilized the electrical properties of the nanonets in ambient conditions. In comparison, SiO_2 provides a better passivation effect due to the compact layer formed at the interface. The large scale NW networks shows acceptable electrical uniformity and provide advantages in flexibility and fault tolerance which makes it amenable for applications in flexible electronics and allow the possibility of fabricating low-cost, transparent, high-performance macroelectronic devices.

Since both water vapor and oxygen adsorption played important roles in the metal oxide FET system, their functions were checked separately. A semiconducting behavior of the device was hardly shown in humid air. The flow-in of dry air decreased the density of free carriers, increased the threshold voltage and demonstrated a better ON/OFF ratio. Moreover, the process is reversible on the time scale of 100s. The results confirmed the additional electrons produced during the water vapor adsorption process. Under white light illumination, 0%O₂ nanonet devices exhibited significant photocurrent response in the controlled environment while there is almost no change in the 0.5% O₂ device, which confirmed the significant role of surface defects in metal-oxide NWs and suggested potential applications of SnO₂ nanonet FETs in gas sensors and photodetectors.

The conductivity of the NWs can be tuned by adding impurities (Sb) into SnO₂ nanonets were studied through contact measurement in a FET and also a non-contact optical approach. The nanonet FET devices exhibit different device characteristics revealing the doping effect, whereas the optical THz-TDS spectra yield more intrinsic physical parameters of the materials due to the absence of extra influence such as contact resistance and junction barriers between NWs. The nanonet FET characterization under varying temperature conditions would provide the important information on the localized/trapped states at inter-wire junctions. While single-crystalline properties were shown in small channel length (20μm) devices, the significant amount of localized/trapped states at the nano-junction sites tended to signify for the polycrystalline nature.

An examination of the photo-excitation process in hybrid NW system indicated that incomplete coverage of P3HT overlayer on NWs enhances the photocurrent by transferring the generated

electrons to the nanonet, making the device function as photodetector. In contrast, a thicker P3HT overlayer allows ambipolar transistor behavior. Control over the morphology and chemical composition by changing the spatial electric field along the deposition region plays a crucial role in modulating the photon-to-current efficiency in CIS/SnO₂ system. In addition, varying the physical properties of NW such as length and diameter has a great impact on the cell efficiency in the dye/nanonet hybrid system.

Summing up, investigations on the electronic property of the pristine metal oxide NWs and hybrid NW systems have been performed extensively. Contact printing allows the NWs to be assembled through simple yet high-yield process and the exciting performance was revealed with good uniformity on large-scale semiconductor device applications. The main focus of the thesis was to understand charge transport in inorganic oxide based nanowire devices. The key findings included an in depth understanding of the role played by growth conditions, growth atmospheres, dopants, nanojunctions, and passivation layers in tin oxide based nanowire networks. These extensive fundamental investigations would lead to establish a solid ground for future exploration of flexible electronics. Hybrid devices combining nanonet devices with photoabsorbers as well as p-channel materials also provide a tool-box for novel functionalities and possible applications towards photodetectors, gas sensors, as well as photovoltaic devices.

In conclusion, crystalline metal oxide semiconductor NWs have demonstrated excellent performance for a broad spectrum of applications. This study addresses the issues involved using a top-down approach for nano-structures allowing their integration over areas compatible to flat panel technology. The effects of a wide range of parameters from growth conditions, nanowire and nanonet dimensions, surface chemistry, doping and transport properties of tin

oxide nanonets are comprehensively investigated in this study. It is rational to conclude that nanonet FETs are more realistic compared to single-nanowire devices in terms of not only fabrication but also for typical applications such as photodetection, chemical or bio sensors, and solar cells. Therefore it is of great pertinence to look at transport properties of entangled nanowires (i.e., nanonet). Nevertheless, cost-effective assembly of NWs remains a bottleneck for large-scale, practical applications. The contact printing of metal oxide nanowires used in this study still needs to be improved in terms of printing nanowires with controlled density and with specific patterns, printing nanowire superstructures, and achieving continuous printing. All these issues are key factors for further scalable device fabrication and integration.

With the rapid development of nanotechnology and increasing attention from industry, it is expected that commercial applications of large-scale metal nanowire transistors will be realized soon.

Chapter 6

RECOMMENDATIONS FOR FUTURE WORK

6.1 Modeling of the nanonet system.

2-D NW network modeling will provide a good understanding about charge transport inside the NW networks. As we introduced, the junctions of crossing NWs play significant role in dictating the semiconducting behavior, sensor response, and that the relationship between the response and NW density can be explained by the percolation theory.

Previous work was mainly focused on the electrical percolation threshold (EPT) in nanocomposites. EPT is known as the critical content of NWs in fillers that characterizes a drastic increase in conductivity. Many theoretical and numerical studies have been carried out were based on different approaches such as continuum mechanics and Monte Carlo simulations(172-173). Similarly, 2-D modeling using Monte Carlo methods or the others can also be designed for numerical studies of the formation of NW networks, the effect of channel length and number of NW-NW junctions, as well as parameters such as the degree of NW alignment (characterized by the FFT ellipticity angle), the nanonet density and orientation, etc. on the electrical performance of nanonet devices.

6.2 All-printed fabrication devices on flexible substrate.

While printing process has been demonstrated for the NW patterned assembly, the device fabrication still relies on the conventional process which requires patterning and metal evaporation. Inkjet or screen printing of the contact and gate dielectrics can be incorporated with the NW printing technology for the demonstration of an all-printed NW circuitry. Printing technology offers the potential for the rapid and inexpensive, large scale manufacture of

electronic devices. The flow chart in Figure 6.1 shows the fabrication process of the all printed electronics based on tin oxide nanonet on flexible substrate. Screen printing technique is used to produce all the layers except the active channel. Briefly, silver (or carbon) electrode was first screen-printed on to the substrate (flexible PET here) following by the transfer printing of tin oxide NWs. BaTiO₃-loaded polyurethane foam was also screen-printed to produce the required permittivity with silver gate was printed finally.

Figure 6.6.1 Illustration of fabrication process of all-printed electronics based on tin oxide nanonet.

Figure 6.2 shows the preliminary data obtained from silver and carbon electrodes respectively. Devices were characterized in ambient and reasonable output characteristics were exhibited for both the approaches. It is worth noting that contact resistance is obvious due to the mismatch of work function between metal electrodes (4.5 eV for Ag and 5.0 eV for C) and tin oxide active channel (4.2 eV), nevertheless, the transfer curves demonstrated ON/OFF ratio of 10^3 with field effect mobility around $1 \text{ cm}^2/\text{V.s}$ (with Ag electrodes). We believe that with improvement of

the metal electrode and fabrication techniques, the electrical performance of devices printed will be significantly improved.

Figure 6.6.2 The output characteristics and transfer curves of all printed field effect transistors: (a)(b) Screen-printed silver electrodes, inset in b shows the integrity of the electrode after NW transfer (PET substrate); (c)(d) Screen-printed carbon electrodes.

In conclusion, using printing to fabricate devices enables purely additive processing techniques which reduces process complexity and allows savings in raw material and manufacturing costs as well as an increase in throughput. In addition, printing which allows the use of polymeric substrates goes well with roll to roll techniques which can bring the manufacturing cost further down. While the fully printed devices are still open to improvement, they are already displaying

viable performance levels. With continuing advances in materials science and printing technology there is every reason to believe that printed electronic devices will form a major part of the rapidly expanding electronics market.

6.3 Circuitry integration and large-scale nanonet-based backplane for flat panel displays

Figure 6.6.3 NMOS inverter based on tin oxide nanonet. Inverter voltage transfer curves and voltage gain plots: (a-b) enhancement mode; (c-d) depletion mode.

Tin oxide nanonet based NMOS inverter has been fabricated and the preliminary data is listed in Figure 6.3, working in both enhancement and depletion mode. W_D/L_D (K_{Drive}) = 2500:300 and W_L/L_L (K_{Load}) = 1500:150 was adopted for the drive and load transistor. Both the sharpness of

the transition region and the minimum output voltage (or the logic 0 level) need to be improved as indicated by the figure. The sharpness of the transition region can be increased by increasing load resistance (as the width-to-length ration of the load transistor decreases, the effective resistance increases). The minimum output voltage for a high input decreases with an increasing K_D/K_L ratio ($K_{Drive} = W_D/L_D$, $K_{Load} = W_L/L_L$). Under this concept, we modified the design as in Figure 6.4 and further modification will be made upon the data collected.

Figure 6.6.4 Schematic of the improved inverter design ($K_{Drive} = 390$, $K_{Load} = 30$).

In addition, a simple 3-inverter ring oscillator will also be designed and fabricated with the ultimate aim is large-scale nanonet-based backplane for flat panel displays.

The Organic light emitting devices (OLED) has emerged as one of the most promising candidates that has the greatest potential in realizing lightweight, high-resolution, full color flat panel display. The traditional display backplane has been fabricated with inorganic semiconductors such as amorphous silicon or poly-silicon technology. Previous work from our group has shown that coupled with organic thin-film transistors (OTFT), an extremely flat and mechanically flexible all-organic display can be realized. The lightweight and rugged OTFT

backplanes with integrated high efficiency OLEDs which forms robust and highly portable active matrix emissive flat panel displays. With the similar design and technology, tin oxide nanonet TFT-OLED integrated backplanes can also become a viable option as it has the potential of producing flexible and transparent display modules.

Essentially, a backplane is an array of transistors that are linked together with interconnecting architecture of metal lines, i.e. gate, source and drain electrodes as shown in Figure 6.5 which is simple 2 transistors/1 capacitor geometry.

Figure 6.6.5 Circuit diagram of a single pixel.

Based on the electrical data obtained including the uniformity testing, backplane matrix of 128 SnO_2 nanonet TFTs that comprise 8x8 pixel active matrix display backplane can be proposed in the starting stage, silicon nitride (PECVD) or BaTiO_3 -loaded polyurethane foam (screen printing) can be adopted as the dielectric and a fully functional FPD can be expected after integration of the encapsulation layer and the OLED element. Failure analysis will be carried out and circuitry defects will be indentified to explain malfunctioning pixels and to improve future efforts in fabrication of metal oxide nanonet TFT backplanes.

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1. **Sun Cheng**, Nripan Mathews, Subodh Mhaisalkar. “Nanowire network based horizontal charge collectors” US Patent Filed with BOSCH;
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Conferences

1. “Metal oxide Nanowire Networks for Transistors and Photovoltaics”, **Presented by colleague** in *MRS Autumn 2010, Boston*; (MRS: Material Research Society)
2. “Field Effect Transistors Formed from Metal Oxide Nanowire Networks”, **Poster** in *MRS Autumn 2010, Boston*;
3. Single Crystalline Zn_2SnO_4 Rhombohedral Nanoplates Growing as Zigzag Nanowires: Synthesis, Crystallochemical and Electrical Characterization. **Presented by colleague** in *MRS Spring 2011, San Francisco*.
4. “Aligned SnO_2 Nanowire Network Based Phototransistors with Potential Application in DSSCs” **Oral Presentation** in *ICMAT Singapore 2011*; (ICMAT: International Conference on Materials for Advanced Technologies)
5. “Mobility Edge in High-Performance Transistors Based on Aligned Tin Oxide Nanonets ”, **Oral Presentation** in *ICACC Daytona Beach 2012*, **Invited** (by Invitation Only); (ICACC: International Conference and Exposition on Advanced Ceramics and Composites)
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7. **Session Chair** for S7: International Symposium on Nanostructured Materials and Nano-Composites in *ICACC Daytona Beach 2012*.

Appendix A

TDS Calculation of electrical parameters

THz pulse passing through material is modified by the reflection and transmission at surface and interface, absorption of the material and dispersion in the material. From the complex amplitude ratio of the transmitted THz pulses from the sample and reference, the complex transmission coefficient, $\tilde{t}(\omega)$, is given as

$$\begin{aligned}\tilde{t}(\omega) &= \frac{\tilde{E}_{sam}(\omega)}{\tilde{E}_{ref}(\omega)} \\ &= \frac{2\tilde{n}(n_s + 1)\exp[i\omega(\tilde{n} - 1)d/c]\exp[i\omega(\tilde{n}_s - 1)d/c]}{(1 + \tilde{n})(\tilde{n} + n_s) + (1 - \tilde{n})(\tilde{n} - n_s)\exp(2i\omega\tilde{n}d/c)}\end{aligned}\quad (1)$$

where $\tilde{n}$ and d are the complex refractive index and thickness of nanonets, respectively. $\tilde{n}_s$ is the refractive index of substrate.

The complex refractive index $\tilde{n}(\omega)$ can be extracted from Equation 1 by numerical iteration, which enables further electrical and optical properties characterization of the nanonets by the following relationships:

$$\tilde{\varepsilon}(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) = \varepsilon_\infty + \frac{i\tilde{\sigma}(\omega)}{\omega\varepsilon_0} = \tilde{n}(\omega)^2 \quad (2)$$

where $\tilde{\varepsilon}(\omega)$ is the frequency dependent complex dielectric constant and $\tilde{\sigma}(\omega)$ is the complex conductivity of the samples, respectively. ε_0 is the free space permittivity and ε_∞ is the high frequency dielectric, $\varepsilon_\infty = 3.8$ for SnO₂. Hence combining Equation 1 and 2, the refractive index (black circle in Figure B1), power extinction coefficient $\kappa(\omega)$ (red circle in Figure B1) which related to absorption

coefficient as, $\kappa(\omega) = \frac{\alpha(\omega)c}{2\omega}$, complex conductivity of the three samples can be obtained and presented in Figure B1 and B2, respectively. It should be noted that, since the nanonets comprise of loosely lying nanowires and nitrogen, the physical properties directly measured from the spectra of THz time-domain waveforms include the contributions of both nitrogen and pure nanowires. To obtain the physical parameters of the pure nanowires, a brief effective medium approximation, $\tilde{\epsilon}(\omega) = f\tilde{\epsilon}_s(\omega) + (1-f)\tilde{\epsilon}_h(\omega)$, where $\tilde{\epsilon}_s(\omega)$ and $\tilde{\epsilon}_h(\omega)$ are the complex permittivity of pure nanowires and the host medium (N₂), respectively. The filling factor $f \sim 0.07$ is obtained from the SEM image.

The far-infrared dielectric response of doped semiconductors are mainly ascribed to free carriers in the frequency range below transverse optical phonon frequency, where the contribution of the polar crystal lattice mode to the dielectric response is negligible. As shown in Figure B1, the refractive indexes of three nanonets decrease with increasing frequency. The calculated refractive index increases with increasing Sb concentration, due to the higher free carrier density with increasing dopant concentration. The far-infrared absorption of semiconductors in THz region is very sensitive to free carrier concentration. The THz wave propagating in semiconductors drives the carriers moving and losing energy by free carriers damping. As shown in Figure B1, the extinction coefficient of doped samples is higher than that of pure SnO₂ nanonets, due to higher free carrier concentration in doped samples. The frequency dependence of refractive index and extinction coefficient are well fitted with Drude-Smith model.

The contribution of free carrier to the optical and electrical properties of semiconductors in the spectral region below the fundamental band gap is determined by the intraband transitions of the partially filled bands. Following the classical dispersion theory, and considering the spatial constraints of free carrier scattering in nanostructures, this intraband transition finally leads to the Drude-Smith theory, for which the complex conductivity is defined by

$$\tilde{\sigma}(\omega) = \frac{\sigma_0}{1 - i\omega\tau} \left[1 + \sum_j \frac{c_j}{(1 - i\omega\tau)^j} \right] \quad (3)$$

where dc conductivity σ_0 is given by $N_0 e^2 \tau / m^*$, N_0 is the electron density, e is the electron charge, τ is the relaxation time and m^* is the electron effective mass. For SnO_2 , $m^* = 0.31m_0$, where m_0 is the mass of free electron. c_j is a parameter describing fraction of the free carrier's original velocity after j numbers of scattering events. Actually, the first term in c_1 is sufficient in describing the normal physical properties and then c_1 varies between -1 and 0, corresponding to a complete backscattering for $c_1 = -1$ and a simple Drude conductivity for $c_1 = 0$.

The measured frequency dependence complex conductivity of the three n-type nanonets with different free carrier concentrations were analyzed using Drude-Smith model, as the solid line shown in Figure B2. Real parts of the complex conductivity gradually increase with increasing frequency, while imaginary parts displaying negative values decreases with increasing frequency. The best fitting parameters are shown in Table B1. Evidently, both the real and imaginary aspects of the complex conductivity can be well fitted by Drude-Smith model, while the samples with higher Sb-dopant concentration present higher conductivity ascribed to higher free carrier concentration. The important parameter, c_1 , indicates large negative values for all of the three samples and fitted as -0.74, -0.85, and -0.91 for sample 1(pure), 2(0.5%Sb), and 3(2%Sb), respectively. The increasing c_1 value with dopant concentration indicates that the localized electrons might experience a preferential backward scattering from defects in nanowires caused by increased structural disorders due to Sb-doping or a Coulombic restoring force ascribed to charged defects. To illustrate this content more quantitatively, the electron mean free path of the three samples at room temperature ($T \sim 300\text{ K}$) were calculated. With an estimated a thermal velocity of

$v = \sqrt{3k_B T / m_0} \approx 1.2 \times 10^5$ m/s, the measured scattering time of 13.7, 6.1 and 5.7 fs for sample 1, 2 and 3 result in the mean free path of 1.64, 0.73 and 0.68 nm, which are much smaller than the average nanowire radius of ca. 60 nm. Therefore, we expect that free carriers would undergo simple Drude-like scattering ($c = 0$) as well as backscattering ($c = -1$) within the nanowires. However, with the dopant concentration increasing, the mean free path of the free carriers decreases dramatically due to the increased structural defects and spatial constraints. The effective electrical parameters of these three samples, free carriers concentration, N_0 , obtained from the best fitting THz-TDS data, electron mobility, $\mu_m = (1+c)(e\tau / m^*)$, dc conductivity, $\sigma_0 = N_0 e^2 \tau / m^*$, were calculated and listed in Table 4.2. Mobility is a phenomenological parameter inferring the carrier scattering rate. It reveals the property of electrons population rather than an individual electron. In FET measurement, the electron states could be populated by free carriers substantially at equilibrium. The field-effect mobility is related to the statistical condition of the carrier momentum relaxation time τ at equilibrium. In the TDS measurement, the carriers studied are in nonequilibrium state, distributing to higher energy states than those at equilibrium or quasi-equilibrium. Their mobility would be determined by the scattering processes and energy relaxation at higher energies where the relaxation time τ is different.

Table B1. Best fitting parameters using Drude-Smith model.

Sample	$\omega_p/2\pi$ (THz)	τ (fs)	c
1	32.9	13.7	-0.74
2	106.6	6.1	-0.85
3	151.2	5.7	-0.91

Figure B1. Measured refractive index (solid black circles) and extinction coefficient (solid red circles) of (a) sample 1(pure), (b) sample 2(0.5%Sb), and (c) sample 3(2%Sb). The theoretical fittings are obtained by Drude-Smith model.

Figure B2. Measured real component (solid black circles) and imaginary component (solid red circles) of complex conductivity of (a) sample 1, (b) sample 2, and (c) sample 3. The theoretical fittings are obtained by Drude-Smith model.

Appendix B*Nanonet devices with channel length range from 15 μm -45 μm*

Figure C1 FE-SEM images of Nanonet devices with channel length range from 15 μm -45 μm with longer NWs.

To further confirm the junction effect, longer nanowires were grown ($>60\mu\text{m}$) and fabricated into nanonet devices (Figure C1). The electrical properties are demonstrated in Figure C2, with $V_{\text{DS}}=5\text{V}$.

As introduced in the previous section (4.1), the electron transport inside nanonet not only comprises intra-wire but also inter-wire (hopping) transport. Increasing the NW length together with reducing the channel length will diminish the nanojunction effect hence intra-wire transport will be dominating part of the carrier transport scheme. It is obvious from Figure C2 that with the channel length decreasing from 45 to 15 μm , the metallic-like behavior becomes more and more prominent which indicates the conversion from inter-wire to intra-wire transport. Figure C3 shows the temperature dependent electrical performance of the nanonet devices.

Figure C2 The transfer curves of devices from Figure C1.

Figure C3 Temperature dependent electrical characteristics of devices from Figure C1. (a-b) I_{ds} vs V_{ds} plots when $V_{gs}=0V$; (c-d) output characteristics (dual sweep) of device with 15 μm channel length.

Appendix C

The output characteristics of tin oxide nanonet FET w/o and w/ dye coating.