Chapter 1

Introduction

1-1　Field emission devices and application

In the past few years, there has been a significant renewal of interest in vacuum microelectronics devices. These new generated vacuum devices have achieved significant progress in their development for applications in ultra-thin flat-panel display devices [1]- [5], microwave amplifier and generator [6]- [8], ultra-fast switching, intense electron/ion sources [9]-[10], micro-SEM, e-beam lithography, micro-sensor [11]-[12] and devices need working in hostile environment, etc. "Vacuum state" devices, in fact, has a remarkable advantages with respect to the prese popular "solid state" devices, including fast drift vel ransit time, radiation hardness and temperature inse le, the "saturation" electron velocity in vacuum is $3x10^{10}$ cm/sec and practically to about 6-9x10^8 cm/sec [13]. In addition, either temporarily or permanently radiation effect should be negligible in vacuum devices due to no medium to be damaged. The effects of temperature on performance are essentially none existent in vacuum devices, such as increased lattice scattering or bulk carrier generation/recombination.

In history, the experimental study of field emission was a very active field of investigation in the 1930's. Later, in 1957, researchers at SRI International began work on what is now called vacuum microelectronics. C. A. Spindt developed a new technology and fabricated a thin film field emission cathode at SRI in 1968. Eventually, he invented the well-known metal field emission cathode called the "Spindt

Cathode" [14]. Figure 1 demonstrates the modern Spindt type field emission triode constructed with a cone-shaped cold cathode and a close positioned extraction gate.
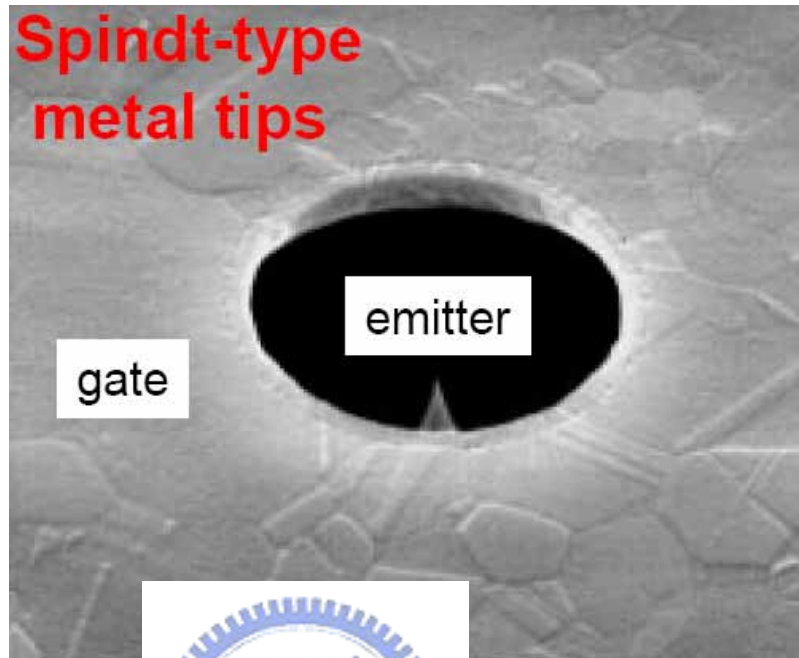

Fig 1 Spi   on structure [15]

Field emission   siderately governed by the Fowler-Nordheim eq   in contrast to thermionic emitters, where refrac   he heated so that some of the electrons in the metal reaches enough thermal energy to overcome the metal/vacuum barrier. Cold cathode operation has two major advantages; first, it eliminates high temperature operation in the electron gun and second, it offers the possibility of extremely long life. Hence, fabrication of the cold emission cathode has become a key issue in the vacuum microelectronics. General requirements of the cold emission cathode are low voltage operation, high current density, small size, compatibility with modern microfabrication techniques and ultra-vacuum processing. For a material with work function of approximately 4.5 eV, an applied field of approximately 10^7 V/cm is needed for electrons to tunnel through the sufficiently narrow barrier [16]. To reach this high field at

reasonable voltage, it is customary to machine the field emitters into protruding objects to take advantage of field enhancement of regions of high curvature. Considering the dielectric films used to isolate the extraction gate and collector electrodes, it is necessary to enhance the protruding emitters for another reason: without field enhancement, the dielectric films would breakdown, since their dielectric strength is below 5×10^6 V/cm. There are many methods of decreasing the voltage applied to the gate electrodes for the field emission [14][17]-[20]. First, making the radius of the emitter tip as small as possible. Second, reducing the separation between the emitter and the gate electrode. Third, employing a low work function material on the emitter. The present availability of microfabrication technologies allows vacuum devices to share the similar micron-size feature with   es. The rapid and extensive development of semic   echnologies could incorporate cold emitters as the ca   potential of close integration.

Up to now, vari   display devices such as liquid crystal display (LC   nt display (EL), vacuum fluorescent display (VFD), and plasma display panel (PDP), organic light emitting display (OLED) are developed. LCDs are by far the most popular flat panel displays. They are successfully used in many portable computers, consumer electronics, and military systems. However LCDs have some drawbacks, such as poor viewing angle and temperature sensitivity.

Compared to the active matrix LCD' s, FED' s generate three times the brightness with greater viewability and temperature range at the same power level. Pixel reports a brightness of 100 cd/m^2 at 1.7 watts for their 6" color displays. Full color FEDs have been developed by various research laboratories from different aspects, which can be roughly divided into two types. One is a high-voltage FED, another is a

low-voltage FED. The color panel consists of three phosphors in each pixel on the anode screen. Appropriate x-y addressibility of cathode allows for addressing the three primary colors individually, or in various combinations, yielding full-color capability. Now, several companies, including PixTech, Futaba, Fujitsu, Samsung, are presently engaged in exploiting FED.

As discussed above, cheap and robust materials for electron sources are still the aim of research and the candidates must have some advantages. For example: smaller the radiu of the emitter tip, reducing the separation between the tip and the electrode to decrease the operating voltage, employing a low work function material on the emitter to increasing emitting current, environment stability and the availability to integrate the present   es As a result, nanomaterial with high aspect ratio   ge manufacturing process has drawn the attenation.

1-2 Nanotecno   nomaterials

The synthesis of the nanomaterials, on a larger scale, represents a paradigm differing from and complementing that of miniaturization by etching (top-down approach) in that they assemble nanostructures from bottom-up (by atoms). If control and rationale formation can be achieved in this paradigm, our capabilities in the nano-world would be fundamentally advanced.

Traditional fabrication techniques such as e-beam lithography can be employed to construct nanorods and nanowires. However, they are generally slow as it requires writing one individual nanostructure at a time. Also, even advanced lithography techniques will find it challenging to reproducibly fabricate structures much

smaller than 50 nm. If this hurdle can be overcome with improved lithographic techniques, there is still the great costs associated with such a technique and the exponentially growing costs of fabricating large numbers of nanorods rapidly and simultaneously over one process run.

Recently, fabrication processes using non-lithographic techniques have been developed to create 1-D nanostructures at a lower cost and can be readily expandable to large volume production. They are vapour based processes and solution based processes. These processes tend to rely on chemical techniques that can synthesize 1-D nanostructures with stringent control over physical dimensions with good reproducibility between fabrication runs. Already, 1-D nanostructures have   GaAs [52]-[53], Ge [54], Si [55], GaN [56], and   a few, by approaches other than traditional litho

Up to now, th   logy has been confined to utilize the smallness   n nanocomposites. However, this may soon change as ongoing research and development have moved towards the explorations of technically crafted nanostructures. This has already led to some remarkable laboratory demonstrations of stand alone nanodevices showing off their unique nanoscale properties. For instance, the motivation of continued miniaturization in the electronics industry led to the demonstration of the single nanotube field-effect transistor [24]. Following that, a single electron transistor was fabricated and characterized [25].

Recently, it was demonstrated that the miniaturization of devices was not confined to electronics with the report of an electrically pumped single nanowire laser [26]. After the initial explorations into single nanostructure devices, the natural progression

is to add complexity and functionality to the devices. In the world of transistors, this led to the demonstration of logic gate functions using a cascade of single nanotube transistors [27]-[28].

Concentrated efforts in the field of zero-dimensional (0-D) and two-dimensional (2-D) nanostructures, such as quantum dots and quantum wells, respectively, have led to significant advances. Ultra-low threshold lasers have utilized quantum dots as their active material, while quantum well devices were employed in many commercial electronic and optical devices. However, one-dimensional (1-D) nanostructures are seen as ideal media for the study of electronic transport as carriers are confined to travel along the axial dimension of the structure. 1-D nanostructures are typically referred to as nanorods, nano   depending on the physical structure. They, by   tropic material with a very large length to diame   etimes exceeding 100 to 1. These 1-D nanostr   orphous, polycrystalline, or single crystal deterr   n methods and conditions used with properties significantly different than in their bulk form. For example, carbon nanotubes combine the characteristics of its two naturally occurring bulk forms, namely its diamond and graphite forms.

Micro emitters have been extensively studied because of promising prospects for many applications such as flat panel displays, cathode ray tubes, and high frequency devices [29]. In order to realize these applications in low power consumption, the emission current must be obtained at a low extracting voltage. For this purpose, the size of the emitter should be decreased and the aspect ratio should be increased. One-dimensional (1D) materials with high aspect ratio make them useful for the better field emission (FE) device. As 1D

emitter materials, carbon nanotube [30], diamond tip [31], and silicon nanowires [29] have been studied.

Field emission (FE) concerning electrons tunneling to the vacuum through a field-modified surface barrier has been extensively studied. The Fowler-Nordheim (FN) theory of FE has been proved to be quite successful in describing electron emission from metallic surfaces.[32]However, to analyze a FE device is often much complicated. Moreover, the applications of the FE devices, e.g., flat panel display (FPD), require emitters exhibiting low turn-on voltage, large FE current density, reproducibility, stability, and good retention and fatigue-resisting properties[33]-[34] among which some of them cannot be explained solely on the FN theory. For example,the sh   affects its FE properties significantly. [35]–[arge aspect ratios, such as carbon nanotubes (C   etter FE properties than the flat samples due to   f the local field. [38] The prototype of CNTs-   thus fabricated. Recently, low-dimensional oxides have stimulated much research interests for their potential applications in FE devices. [39]- [40] Compared with CNTs, oxide emitters are more stable in harsh environment and controllable in electrical properties. [41]-[43] As a wide band-gap semiconductor, ZnO exhibits many fascinating electrical and optical properties. It can be n-type doped with nitrogen or simply through oxygen vacancies to reach a high carrier (electron) density, which can support a large electron disbursement in FE operation, i.e., a large emission current. [44] Furthermore, ZnO nanoneedle arrays have been successfully fabricated recently. [45]-[46] The high aspect ratio of the individual nanoneedle and the good alignment between the nanoneedles can dramatically enhance the local

electrical field and thus increase the emission current.

Up to now, the physics of the high FE performance of the ZnO nanostructures still remains unclear. Dong et al. proposed that the high FE originated from adsorbates and the emission followed FN relation in the case of single ZnO nanowire emitter, [49] whereas, in general, the effect of adsorbates on the FE properties are also ambiguous. For the CNT emitters, different experimental results and theoretical models concerning adsorptions including the space charge [50] and cathode adsorption models [51] have been proposed.It is hence worthy to investigate the adsorption induced phenomena for ZnO emitters in the viewpoints of both fundamental physics and advanced technology. In other words, the effects of cathode adsorbates   perties of ZnO nanoneedle arrays need to be co

In this diss   npted to fabricate 1-D nanostructures and d   nethods for the assembly of nanostructures into p   mparing to CNTs, we chose to study ZnO nanorods, a material system with great potential for impact in a wide range of fields.

1-3 ZnO material properties and applications

Zinc oxide (ZnO), or sometimes known as zincite in mineralogy, was first described in North America around 1810 as the red oxide of zinc. In its pure form, ZnO has a silvery-grey colour, however, in its most natural states, a deep dark red tint is typically observed given by the small deposits of manganese (Mn), typically less than 7% by weight, in the specimens. The mineral has mistakenly been called ruby due to its complexion and is referred to as "ruby zinc".

ZnO can take the form of two different crystallographic structures namely the zinc-blende structure and the wurtzite structure. The zinc-blende structure is composed of two interpenetrating face-centered cubic (fcc) sub-lattices, while the wurtzite structure consists of two interpenetrating hexagonal close packed (hcp) sub-lattices. The two sub-lattices, fcc and hcp, are shown in Fig. 2. Each Zn is surrounded by four O atoms forming a tetrahedron and at any point in the lattice, the nearest neighbours are identical.

The wurtzite crystal structure has a hexagonal unit cell and therefore is defined by *[hkil]*. The first three coordinates use three vectors forming a 120° angle with each other in the basal plane.
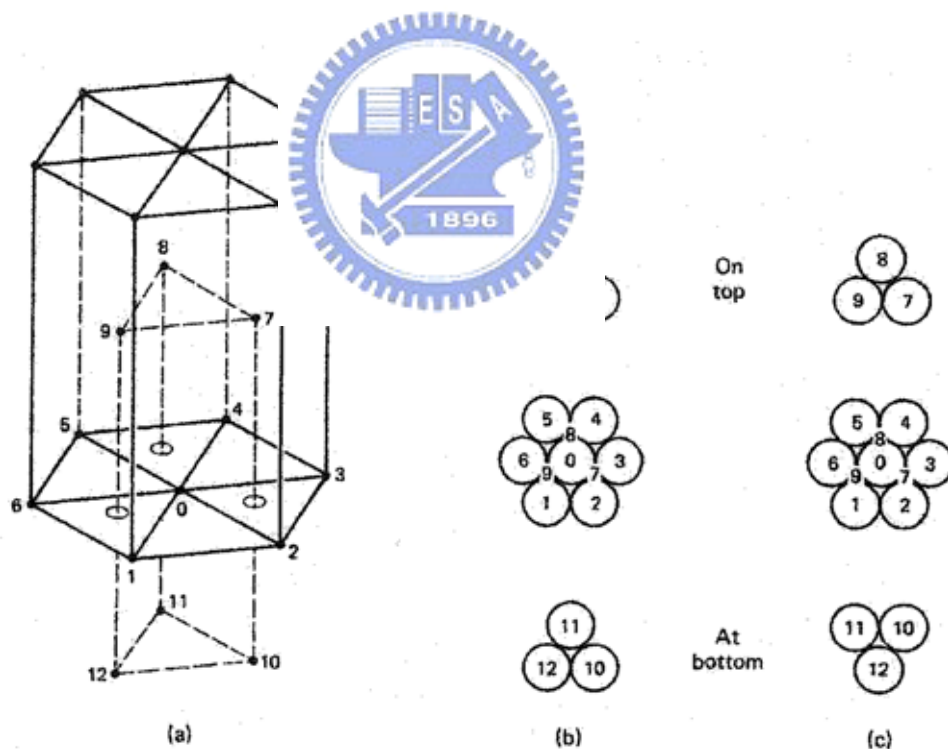
Fig. 2 Composition of (a) the hexagonal close-packed structure, with the arrangement of atoms in three consecutive layers in the (b) hcp structure, and (c) fcc structure from [58].

As the three vectors are not independent of each other, only two

vectors are necessary to provide enough information to describe the system. The third index can be used as a check as,

$$h + k + i = 0 \qquad (1\text{-}1)$$

But we also use three vectors to indicate the plane direction and their relation are

$$U = h - i, \; V = k = i, \; W = l \qquad (1\text{-}2)$$

The predominant structure for ZnO is the wurtzite crystal shown in the model in Fig. 3. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis.
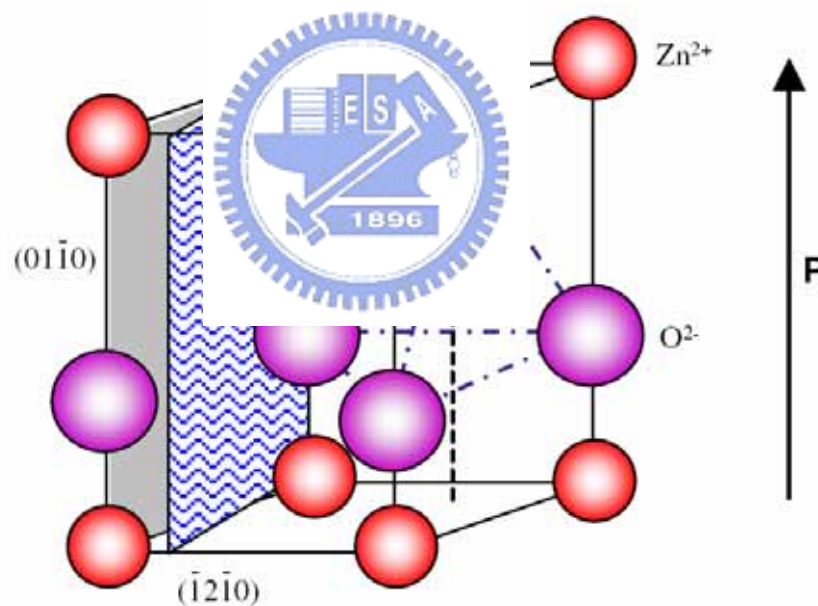
Fig. 3 wurtzite structure of ZnO and its polar direction [59]

The tetrahedral coordination in ZnO results in noncentral symmetric structure and consequently piezoelectricity and pyroelectricity. Another important characteristic of ZnO is polar surfaces. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged Zn-(0001) and negatively

charged O-(000$\bar{1}$) surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis as well as a divergence in surface energy.

Since the lattice structure between zinc-blende and wurtzite crystals are different, the bandgap energies are also found to differ. The bandgap of zinc-blende ZnO has been found to be smaller than wurtzite ZnO by 0.08 eV from theoretical calculations [66], and by 0.10 eV from experimental data [67]. A common characteristic of wide bandgap semiconductor materials is the difficulty to dope the material p-type. GaN can be doped p-type with the addition of Mg acceptors; however, the energy levels are still 150 meV above the valence band resulting in a room temperature activation of only 3% of the dopants. Some   operties are listed in Table 1.

Property	Value
Lattice parameters	
a_0	0.324 95 nm
c_0	0.520 69 nm
a_0/c_0	1.602 (ideal hexagonal structure shows 1.633)
u	0.345
Density	5.606 g/cm^3
Stable phase at 300 K	Wurtzite
Melting point	1975 °C
Thermal conductivity	0.6, 1−1.2
Linear expansion coefficient(/C)	$a_0 : 6.5 \times 10^{-6}$ $c_0 : 3.0 \times 10^{-6}$
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Energy gap	3.4 eV, direct
Intrinsic carrier concentration	$<10^6$ cm^{-3}
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron Hall mobility at 300 K for low n-type conductivity	200 cm^2/V s
Hole effective mass	0.59
Hole Hall mobility at 300 K for low p-type conductivity	5−50 cm^2/V s

Table1. ZnO Material Properties [68]

ZnO is also a direct wide band gap semiconductor. This automatically makes it a good candidate for radiative recombination. The fact that it has a bandgap of 3.37eV making it a potentially important material. Its energy band relationship to other materials is shown in Fig. 4.
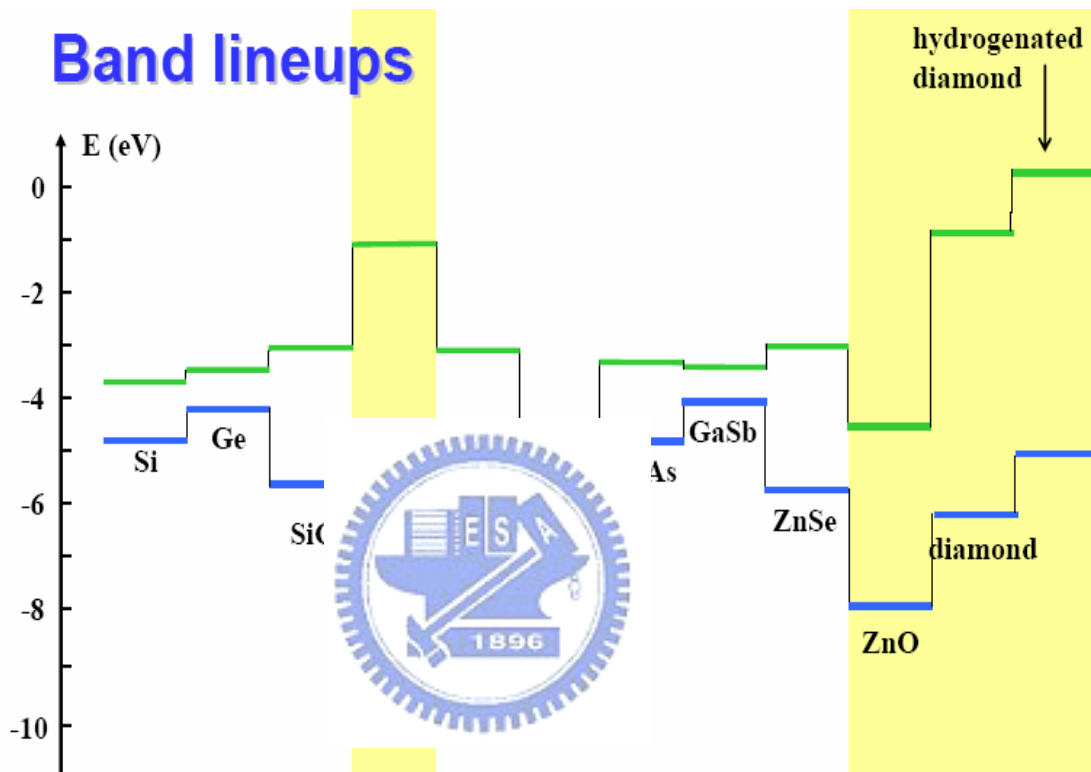

Fig. 4 band lineups of different materials[59]

Many applications to date use these wide bandgap materials for light sources. For instance, the use of shorter wavelength light emitting diodes (LEDs) when compared to conventional red line in the read and write heads of CD players and first generation DVD players has been demonstrated to increase storage capacity as each bit will take up less real estate. Although up to now, GaN has been the material of choice, ZnO has one significant advantage. The room temperature exciton binding energy for ZnO is 60 meV, while it is only 27 meV for GaN. Excitons generally refer to bound

states of an electron and a hole interacting with each other. Considering the thermal energy at room temperature is about 26 meV, the probability that excitons will recombine due to thermal excitations is exponentially smaller than for GaN given the binding energy being 2.6 times higher than kT, where k is the Boltzmann's constant and T is the temperature. This is especially important for lasing as these excitons have a greater chance to contribute to the stimulated recombination process, rather than in a spontaneous recombination process, thus potentially leading to lower current thresholds. Also, ZnO devices will be able to operate at higher temperatures and at higher powers with minimized regards to thermal noise.

Up to now, th   of ZnO is in its thin-film form. Since the ma   in the visible wavelength range and is highly c   oper doping, ZnO thin films used as transparent   s in optoelectronic devices play a role similar to   ide (ITO) does for UV/blue vertical cavity surface emitting lasers (VCSELs). ZnO thin films have been used as the front contacts to Si solar cells [69]-[70]. Gas sensors application using ZnO thin films has also been studied due its the efficient interactions with gases such as oxygen and dangerous gases such as ammonia [71] and nitrogen oxide [72]. ZnO thin films on its own have been demonstrated as surface acoustic wave devices [73] and as lasers when optically pumped [74]-[76]. Investigations into ZnO nanoparticles have also mainly focused on its optical property and its prospects of lasing [77]-[78]. Besides pure ZnO film, its large direct bandgap has the availability of heterostructures with Ca or Mg addition to increase or decrease bandgap, and is piezoelectric and pyroelectric. These properties make it attractive for

applications in gas sensing, surface acoustic wave devices, and transparent thin-film transistors for displays [79]–[84].

ZnO also readily forms a large variety of one-dimensional nanostructures [85]–[104]. The large surface area afforded by arrays of nanorods and their biocompatibility makes them attractive for sensing applications [105]–[107]. In recent years, one-dimensional (1D) ZnO nanostructure, such as nanowire, nanorods, nanobelts and nanotetrapod, have attracted much attention [108]–[112]. It is experimentally demonstrated that ZnO nanorods show a promising application for humidity sensors.

The humidity control is essential for various fields of industry as well as human life. There is a substantial interest in the development of hu   application in monitoring relative humidity (R   itive environment (such as glove boxes and cle   of trace moisture in many types of pure ga   uctor manufacturing and packaging, cryoge   lical and food science application, and so on. Several transduction techniques have been explored, for example, changes in the capacitance and resistance of polymer and ceramic materials, in the oscillation frequency of thin piezoelectric quartz plates and in the luminescence of microporous silicon, which are being used to measure humidity levels [113]-[114]. The desirable characteristic of humidity sensors are high sensitivity, chemical and thermal stability, reproducibility, low operation temperature, low cost and long life. So far, however, there has been no optimum material that could fulfill all those requirements simultaneously [115]–[118]. ZnO is a versatile II–VI semiconductor with numerous applications ranging from optoelectronics to chemical sensors because of its distinctive

optical, electronic and chemical properties. It is well known that dimension or the surface-to-volume ratio has great influence to the material performance.

1.4   Motivations and organization of dissertation

All of the remarkable nanotechnology achievements presented began with demand knowledge from the material properties. In this dissertation, we attempted to fabricate 1-D nanostructures and developed a suite of methods for the assembly of nanostructures into practical devices. Comparing to CNTs for the FED application, we chose to study ZnO nanorods: a material system with easy preparing process, st   , environment stability and great potential for in   of fields.

The fabricatio   emiconductor nanowires in well-controlled wa   of the most important challenges in bu   nanoelectronic devices. Metal-catalysts, such as gold, cobalt and nickel, have been used to prepare ZnO nanowire arrays on insulating sapphire through a vapour–liquid–solid (VLS) growth process [119]. However, the metal catalysts might remain the contamination when integrating with other Si base devices. As a result, growth of ZnO nanorod without catalyst and mechanism are important.

In Chapter 2, we demonstrate for the first time the feasibility of growing single crystalline ZnO nanorods on porous silicon (PS) without any catalyst. The growth and characterization of the ZnO nanorods are also demonstrated in detail. Moreover, the probable growth mechanism of ZnO nanorods on the PS surface is examined.

In the pursuit of next generation ZnO based optoelectronic

nanodevices (e.g. gas sensors and UV detectors, etc), it would be highly desirable if well-ordered ZnO nanorods could be aligned onto conducting and cheap substrates, such as Si wafers, to integrate for more application. Different methods have been reported for the synthesis of well-aligned ZnO nanorod arrays, which include template methods[120]-[121], vapor transport and condensation methos [122]-[123],metal vapor deposition methods [124]-[125] and metal-organic source vapor deposition [126]-[127]. But template methods usually utilize anodic aluminum oxide to grow ZnO nanrods in nanosize channels, and such fabricated nanrods are normally polycrystalline. Besides the method is not compatabile with semiconductor process and the contamination still remains.

In chapter 3   ple bottom-up fabrication technique based on   ) growth method with the standard and low-   thography technique. The techniques with prope   gas can selectivly grow the single ZnO nanorods on Si-substrate. The field emission (FE) properties of the patterned ZnO nanorods were carried out and the screen effect of FE was also demonstrated under different density of nanorods.

Recently, the FE of graphitic ribbons was investigated by Tada and Watanabe using the time-dependent density functional theory (TD-DFT).[128] They found that the dangling-bond states and not the edge states contribute primarily to the FE. They also found that not only evaluation of work functions but also knowledge of local electronic properties is prerequisite for understanding the microscopic mechanisms of FE properties of covalently bonded nanostructures. Tada and Watanabe's results cannot be derived from the conventional

Fowler-Nordheim theory for the FE from flat jellium surfaces with the free-electron approximation.

In Chapter 4, the affected effect from defect of ZnO nanorod was studied. First, the existed oxygen vacancy might affect the work function of ZnO which might result in the different FE properties. Moreover, we explored the blue-emission of ZnO nanorod under field emission induced lumincence, named Field Emission emitted lumincence (FEEL). The reason might be the recombination of oxygen vacancy.

But the large differences in their thermal expansion coefficients and lattice mismatch causing a rather large stress between ZnO and the Si wafer.

Synthesis of nanorod arrays on Si is of great interest because ant step towards realizing nano-optoelectronic on physics. With the same patterned ZnO nano and scanning capacitance microscopy (SCM) physical properties of the ZnO nanorods. In Chapter 5, we began the exploration of assembling the nanorods into nanodevices. We characterized the Schottky junction and n-ZnO/p-Si heterojunction through I-V and C-V measurement and the discontinuity of band offset was also demonstrated. Moreover, the interface state was also considered to explain the C-V properties due to the existed oxygen vacancy stated in Chap 4.

For the future coupled with the developments in this thesis, new methods and devices can be design. The sited controlled process on Si substrate is demonstrated opening up the window of many novel functional devices in optoelectronic integrated devices.