STRUCTURE AND ELECTRICAL PROPERTIES OF GALLIUM ARSENIDE NANOWIRES GROWN BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION

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Faculty of Science
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To my beloved husband and childrens
ACKNOWLEDGEMENT

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ABSTRACT

Gallium Arsenide nanowires (GaAs NWs) have been grown on GaAs and Silicon (Si) substrates by gold-assisted and using metal-organic chemical vapor deposition (MOCVD) method. The structural properties and electrical conductivity were studied and was found to be strongly dependent on the pre-annealing temperature, growth temperature, growth period and V/III ratio. Pre-annealing process at 600 °C has produced an eutectic point of Au and GaAs substrate and initiated the growth of the NWs. The NWs were uniform in diameter and composition at a growth temperature of 460 °C, growth period of 30 minutes and V/III ratio of 166. Activation energy for the NWs in the temperature range (420 – 480) °C was found to be 58.86 kJ/mol. Energy dispersive X-ray analysis (EDX) indicated the presence of Au, Ga and As. From the field-emission scanning electron microscopy (FE-SEM), the growth of the NWs were at an elevation angle of 90°, 60°, 65° and 35° with respect to the GaAs substrate for (111)B, (311)B, (110) and (100) orientations respectively. The NWs grew vertically, randomly and horizontally on the Si(100) substrate when there was no pre-annealing process, pre-annealing process at a temperature of 600 °C for 10 minutes and an extended pre-annealing process at 450 °C for 7 minutes respectively. High-resolution transmission electron microscope (HRTEM) micrograph showed the NWs that grew on the GaAs(100) substrate has less structural defects when compared to the GaAs(111)B. The electrical conductivity of the NWs from the measurement of the conductive atomic force microscope (CAFM) showed similar to that of a p-n junction characteristics. The energy gap for the GaAs NW was found to be 1.50 eV.
ABSTRAK

Dawai nano Galium Arsenida (GaAs) telah ditumbuhkan di atas substrat GaAs dan Silikon (Si) dengan bantuan zarah emas dan menggunakan kaedah pemendapan wap kimia logam organik (MOCVD). Kajian sifat struktur dan kekonduksian elektrik menunjukkan dawai nano GaAs sangat bergantung kepada suhu pra-sepuhlindap, suhu pertumbuhan, masa pertumbuhan dan nisbah V/III. Proses pra-sepuhlindap pada suhu 600 °C menghasilkan titik eutektik antara Au dan substrat GaAs, dan mula merangsang penumbuhan dawai nano. Diameter dan komposisi yang seragam pada dawai nano diperolehi pada suhu pertumbuhan 460 °C, masa pertumbuhan 30 minit dan nisbah V/III 166. Tenaga pengaktifan dawai nano pada julat suhu (420 – 480) °C adalah 58.86 kJ/mol. Analisis tenaga pembelauan sinar-X (EDX) menunjukkan kehadiran Au, Ga dan As. Melalui kajian pancaran-medan mikroskop imbasan elektron (FE-SEM), dawai nano GaAs tumbuh pada sudut kecondongan 90°, 60°, 65° dan 35° terhadap permukaan substrat GaAs dengan masing-masing orientasi (111)B, (311)B, (110) dan (100). Dawai nano tumbuh secara menegak, rawak dan mendatar di atas substrat Si(100) masing-masing apabila tiada proses pra-sepuhlindap, pra-sepuhlindap pada suhu 600 °C selama 10 minit dan pra-sepuhlindap tambahan pada suhu 450 °C selama 7 minit. Mikrograf mikroskop pemancaran elektron resolusi tinggi (HRTEM) menunjukkan dawai nano yang tumbuh pada substrat GaAs(100) kurang struktur cacat berbanding substrat GaAs(111)B. Kekonduksian elektrik dawai nano daripada pengukuran mikroskop konduktif daya atom (CAFM) menunjukkan kesamaan terhadap pencirian simpang p-n. Jurang tenaga dawai nano GaAs yang diperolehi adalah 1.50 eV.
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LIST OF SYMBOLS

\( a \) - Lattice parameter
\( A \) - Actual device area or contacted
\( A^* \) - Effective Richardson’s constant for semiconductor crystal
\( \alpha \) - Specific surface free energy of the NW surface
\( b \) - Coefficient independent of saturation
\( \beta_0 \) - Contact angle
\( d_c \) - Critical diameter of NW
\( d_w \) - Diameter wire
\( e \) - Electron charge
\( E_a \) - Activation energy
\( E_c \) - Conduction energy
\( E_F \) - Fermi energy
\( E_{F(o)} \) - Fermi level at equilibrium
\( E_{Ff} \) - Fermi level
\( E_g \) - Energy bandgap
\( E_v \) - Valence energy
\( I \) - Current measured
\( I_s \) - Saturation current
\( k \) - Boltzmann constant
\( l_w \) - Carrier mean free path
\( m \) - Electron mass
\( m_o \) - Free electron mass
\( n \) - Ideally factor
\( r_o \) - Initial radius of the contact area
\( r \) - Radius of the contact area
R - Gas constant
s - Tip-sample separation
T - Absolute temperature
τ - Line tension
τ_c - Effective chemical tension
V - Applied bias voltage
Ω - Atomic volume of reactants
χ - Electron affinity
σ_{LS} - Surface tension liquid-solid
σ_{LV} - Surface tension liquid-vapour
σ_{VS} - Surface tension vapour-solid
σ_{ls}^c - Effective surface tension
l_0 - Elementary thickness
η - Vapour source of the actual-to-equilibrium pressure ratio
σ_c - Chemical tension
Δμ - The difference in chemical potential of reactant in the vapour phase and in the wire
Δμ_o - The difference in chemical potential of reactant in the vapour phase and in bulk
λ_e - de Broglie wavelength of electron
dI/dV - Conductance
ρ_s(E) - Surface DOS for sample
ρ_t(E - eV) - Surface DOS for tip
T(E, eV) - Transmission function for tunnelling electrons
Φ_B - Schottky barrier height
φ - Work function
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<tr>
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<th>Description</th>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>Au</td>
<td>Aurum</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic</td>
</tr>
<tr>
<td>AsH₃</td>
<td>Arsine</td>
</tr>
<tr>
<td>CAFM</td>
<td>Conductive Atomic Force Microscopy</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
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<tr>
<td>CH₄</td>
<td>Methane</td>
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<tr>
<td>DOS</td>
<td>Density of State</td>
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<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
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<tr>
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<td>FE-SEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
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<tr>
<td>Ga</td>
<td>Gallium</td>
</tr>
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<td>GaAs</td>
<td>Gallium Arsenide</td>
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<td>Hydrogen</td>
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<td>Liquid-surface</td>
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<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
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<tr>
<td>MO</td>
<td>Metal-Organic</td>
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<tr>
<td>MOCVD</td>
<td>Metal-Organic Chemical Vapour Deposition</td>
</tr>
<tr>
<td>MOVPE</td>
<td>Metal-Organic Vapour Phase Epitaxy</td>
</tr>
<tr>
<td>PLL</td>
<td>Poly-L-Lysine</td>
</tr>
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<td>Rh</td>
<td>Rhodium</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>Transmission Electron Microscopy</td>
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<td>TMGa</td>
<td>Trimethylgallium</td>
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<td>Acronym</td>
<td>Description</td>
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<td>TMIn</td>
<td>Trimethylindium</td>
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<tr>
<td>VB</td>
<td>Valence Band</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapour-Liquid Solid</td>
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<tr>
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<td>X-Ray Diffraction</td>
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<tr>
<td>WZ</td>
<td>Wurtzite</td>
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<td>ZB</td>
<td>Zincblende</td>
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CHAPTER 1

BACKGROUND OF RESEARCH

1.1 Introduction

Nanotechnology is one of the fastest growing and most dynamic areas of research in this decade. The growth can be felt with the emergence of increasingly smaller electronic equipment such as smaller and higher performance computer notebooks, handphones with sizes as small as two fingers, and slim but accessorised with many applications, and many more electronic equipments. Similarly, the information of a library can be loaded into the portable hard drives as the size of a quarter of A4 size paper. For that reason, the quantity of raw materials necessary for functioning devices and power consumption has been decreased. The cost required for an operation will be reduced. The waste released into the air will be reduced when the materials used decrease. Hence, this will trim down the release of carbon dioxide into the environment and will save the earth. Malaysia is also actively promoting the green earth. So as not to be left behind in the modernisation and without missing the flow of life to enjoy the sophisticated and advanced technology, many nano-based researches have been and are being actively carried out. This is reflected in the establishment of centres such as Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, Institute of Science of Universiti Teknologi Mara, Nanocomposite Center of Universiti Putra Malaysia, Institute for Nano Electronics Engineering of Universiti Malaysia Perlis and many others.
The original idea of nanotechnology was presented by a physicist, Richard P. Feynman in 1960 in his famous talk “There’s plenty of room at the bottom” (Feynman, 1960). Nanotechnology is the study and fabrication of devices on the nanometer scale \((10^{-9})\), where one nanometer is one billionth of a meter. One nanometer is approximately the length equivalent to 10 hydrogen or five Si atoms aligned in a line (Guozhong, 2005). The novel materials and devices made on nanoscale offer unique and entirely different properties and applications as compared to conventional technology. Materials in the microscale mostly exhibit physical properties the same as that of bulk form. However, it is different in the nanoscale. For example, the melting point of Au nanoparticle is lower than that of bulk Au since it reduces lattice constant and number of surface atoms and becomes significant in the thermal stability. Size effects become important when at least one dimension of a crystal is reduced to the order of hundreds of atoms which is the length scale of nanometers. This has instigated the explosive growth of the fields of nanoscience and nanotechnology.

Many of the results in nanotechnology today are focused on applications of semiconductor materials. Semiconductors are materials in which the electrical conductivity depends on applied energy such as temperature due to the electronic band structure of the material. The band gap between energy bands is sufficiently narrow and the movement of electrons into the next energy band may occur with a reasonable probability. This allows the materials to conduct electricity when sufficient energy is supplied. This thesis focuses on GaAs materials which is the III-V semiconductor compounds. It has a direct band gap \((1.43 \text{ eV})\) meaning that electrons and holes can combine directly while conserving momentum, a process that results in the emission photon (Brozel and Stillman, 1996) and applicable for optical applications (Lieber, 2003). The mobility carrier of GaAs is very high which is \(8500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) (Wang et al., 2008) compared to Si, which make it ideal for high frequency electronic applications (Lauhon et al., 2004 and Haraguchi et al., 1992).

Nanomaterials are commonly classified according to their dimensionabilities as zero dimensional (dots), one dimensional (nanowires (NWs), nanotubes and nanobelts) and two dimensional (thin films). These categories refer to the number of dimensions in which the material is outside the nano regime (Wang, 2003). Much
work has been focused on the development and application of thin films and quantum dots (QDs) compared to NWs. The formation and properties of thin films are now well-understood, and these materials form the cornerstone of many high-precision products including commercialized lasers, silicon microelectronics and NASA quality optical components (Baca and Ashby, 2005). QDs are also easily synthesized through wet chemistry and aerosol spray, and have been developed in the past few decades into a host of commercial applications such as QD lasers and single electron transistors (Coleman, 1997). Many researchers traditionally have not pursued research into NWs due to their complex and corresponding lack of control over their synthesis. However, NWs have grown and synthesis techniques have greatly improved with the increasing of publications in NWs in the last ten years. The potential for use in commercial environment, electronic and biological applications have increased interest researchers from almost all science disciplines and even to general public. Yet, the formation of NWs is incomplete, limited control and contains structural defects. Also, an understanding of the basic process of NWs has not fully understood and still in debate.

1.2 Semiconductor Nanowires

In the production of semiconductor NWs that meet the criteria of an electronic device, epitaxial growth of NWs need to be highlighted. The tiny, wire-shape structures with diameter less than 100 nanometers and length greater than 1 micron are effectively NWs. The other requirement for the future advanced industrial application of NW materials are straight NWs, uniform in compositional and uniform diameters.

Various techniques have been used to synthesized GaAs NWs such as metal-organic chemical vapour deposition (MOCVD) (Hiruma et al., 1995; Hannah et al., 2008 and Paiman et al., 2009), molecular beam epitaxy (MBE) (Ihn et al., 2007a; Plante and LaPierre, 2008) and chemical beam epitaxy (CBE) (Persson et al., 2004). GaAs NWs are commonly growth using vapor-liquid solid (VLS) technique by applying metal Au as catalyst to initiate crystal growth. The VLS method was first
discovered by Wagner and Ellis (1964). Due to the presence of the metal on the substrate, the geometry and atomic structure of the interface have been found to be very critical to the NW growth. By regulation and preparation of the atomic structure of interfaces, it can help produce high quality NWs.

Annealing temperature plays an important role in the eutectic alloy generated of Au nanoparticle catalyst and substrate surfaces. In the eutectic phase, Au nanoparticles can absorb vapours from the vaporization of the organic materials to form NW crystal underneath the droplet particle. If the Au is in the solid phase, it will not absorb any material and NW crystal did not occurred. Investigation of the annealing process has already been done by many researchers in the formation of GaAs NWs (Seifert et al., 2004; Wang et al., 2008 and Ghosh et al., 2009). However, many studies and observations of colloidal gold particles on GaAs substrate at the early stages of formation were given less attention. Kawashima et al. (2008) has reported the initial stages of Si NWs growth using transmission electron microscopy (TEM). Other groups reviewed on the initial formation of Au catalyst on the surface of the GaAs substrate using TEM and XRD (Ghosh et al., 2009; Mariager et al., 2010). Atomic force microscopy (AFM) morphological studies of the surface characterization of eutectic Au/Ga interface is rarely been done. AFM can image surface structures down to atomic size near native conditions i.e, without capping the sample the conductive layer.

An interesting subject in the VLS growth of NWs is changing their crystalline orientation. Typically, the commonly used GaAs(111)B substrate results in III-V semiconductor NWs grown in to the [111]B direction. This has been reported by several groups in the growth of GaAs NWs (Hiruma et al., 1993 and Borgstrom et al., 2004), InP NWs (Bhunia et al., 2004) and InAs NW (Dayeh et al., 2007a). Important features found in the study of NW when it is grown in the [111] orientation is a high density of twin stacking faults than growing in other orientation. Moreover, NWs also crystallise in a hexagonal structure with higher grown temperature and higher V/III ratio. Thus, from the perspective of quality crystal produced, the NW growth with orientation other than [111] would be beneficial. One method that can be used to change the direction of NW growth is by using different substrate orientation. There are several problems that may arise as result of
different substrate orientation such as catalyst particle annealing (Krishnamachari et al., 2004) and chemical treatment of the substrate surface (Ghosh et al., 2009), which can affect the substrate surface. On the basis of energy consideration, Wang et al. (2008) concludes that the (111)B direction is favourable as it minimises the surface free energy of the liquid-solid interface.

In previous studies of GaAs NWs using MOCVD, mostly dealt with only much thicker NWs (Hiruma et al., 1995; Hannah et al., 2007 and Dick et al., 2010). A fundamental question remains on GaAs NWs, that is the minimum diameter of the crystal NW which is attainable by the growth method. In order to address the question, the growths of GaAs NWs are needed to study quantitatively. By applying the Gibbs-Thomson effect, the growth rates of GaAs NWs have to be plotted with variable diameters of NWs. It is found that GaAs NWs of smaller diameters are likely to grow slower than those of larger diameters. The critical diameter which is the minimum diameters of GaAs NW can be calculated from the plotted graph.

Si(100) substrate is widely used as a substrate in electronic industry for the formation of resonant tunneling diodes (RTD) (Tan et al., 2004a), light emitting diodes (Roest et al., 2006) and solar cells (Jayadevan and Tseng, 2005). The application of NWs in the devices requires the fabrication of materials in the form of horizontal to the substrate surface. Kang et al. (2010) in their studies had grown GaAs buffer layers on Si substrate to minimize the lattice mismatch and by adding the annealing temperature to the layer, the surface structure are formed in quality. Horizontal growth of GaAs NW parallel to substrate offer a benefit of fabricating integrated nanodevice arrays, but there are only a couple of reports about the growth of laterally aligned NWs. Until now, there are a few studies on the horizontal growth of Ga$_2$O$_3$, ZnO and In$_2$O$_3$ NWs on sapphire and Si substrates (Kuo and Huang, 2008; Nikoobakht et al., 2004 and Hsin et al., 2007), but essentially no reports describing the direct horizontal growth of GaAs NWs on a substrate surface using MOCVD method.

Characterisation of nanostructures is a challenging task because of the very sensitivity required due to high surface to volume ratio. Although additional characterisation tools are required to fully understand the chemical and structural
details of the chemical defects, electrical testing can provide a snapshot of the underlying defects in the material. The uses of conductive atomic force microscopy (CAFM) in nanoscale semiconductor devices are preferred because the conductivity of any point can be measured by only probing the AFM tip in a few nanometers distance from the surface. With the probe tip diameter of approximately 100 nm, the conductivity of the material is measured more accurately as compared to the conventional I-V measurements (Yanev et al., 2009). Accordingly, by using excess CAFM, the electrical conductivity of horizontally grown GaAs NW can be measured effectively, especially in different structures of the surface.

The electrical properties of NWs are critically dependent on their dimensions and crystal structure (Dayeh, 2010). Small changes in the diameter of a NW can significantly influence the separation of electronic energy states within the wire owing to quantum confinement. Conductivity variations of this magnitude reflect significant differences in dopant or defect concentrations in the wires. III-V semiconductor NW, which is grown via VLS technique often contain numerous stacking defects composed of ZB and WZ GaAs phase region (Banerjee et al., 2006). These defects may influence the luminescence spectrum (Adu et al., 2006) and may increased resistivity due to increasing the number of carbon-related impurities (Thelander et al., 2010).

1.3 Problems Statement

GaAs NWs is one of the most fascinating III-V semiconductor NWs to be further investigated for application in electronic and optoelectronic devices due to their direct bandgap and higher mobility carrier (Lauhon et al., 2004; Wang et al., 2008 and Lieber, 2003). For the fabrication of NWs, a small size is not the only requirement. For any practical application, the processing conditions need to be highly controlled in such a way that the resulting NWs achieved the desired and quality crystal structure with identical size (uniform size distribution), identical shape or morphology and identical chemical composition.
Previous reports on GaAs NWs, however, still exhibit non-uniform morphology such as tapering and high density of structure defects that should be avoided (Hiruma et al., 2006; Borgstrom et al., 2007 and Ihn et al., 2006). Thereby a well-controlled NW growth process with appropriate growth parameters must be done in order to achieve GaAs NWs with uniform diameters and chemical composition, less defect structure and higher electrical conductivity. Hence, this study will be conducted in order to investigate the effect of variable growth parameters on structural and electrical conductivities of GaAs NWs. Optimum growth parameters and growth control will be selected in order to produce high quality GaAs NWs.

1.4 Research Objectives

There are four objectives outlined in this thesis as follows:

i) to determine the effect of growth parameters i.e; annealing temperature on gold colloids, growth temperature, growth period and V/III ratio on the growth structure of GaAs NWs using MOCVD.

ii) to investigate the effect of annealing temperatures of gold colloids on the growth direction of GaAs NW

iii) to characterize the effect of substrate orientation to the structure of GaAs NWs

iv) to obtain the energy band gap of GaAs NWs from electrical conductivity measurement using CAFM.

1.5 Research Scopes

This thesis focuses on the structural and electrical properties of GaAs NWs grown on GaAs(111)B, GaAs(311)B, GaAs(110), GaAs(100) and Si(100) substrates by VLS mechanism. GaAs NWs were grown using vertical flow MOCVD that is
using purified hydrogen, H₂ as a carrier gas to transport the precursor materials. Substrate was first treated with gold colloids as catalyst to initiate the growth of NWs. The growth parameters addressed in these studies are growth temperature in the range of 380 – 600 °C, growth period (10 – 60 mins), V/III ratio (17 to 297) and substrate of different orientation. The metal-organic source was trimethylgallium (TMGa) and organo-substitude hydride (AsH₃) was used as group V source. Annealing temperatures are deeply studied for the formation of NW structures by changing the process of annealing temperature on gold colloids particle.

Field emission scanning electron microscopy (FE-SEM) was used to visualise very small topographic details on the substrate surface and GaAs NW itself whether in plan view or in cross-section. Energy dispersive X-ray spectroscopy (EDX) was used to measure the changes in elemental composition of gold colloid particles, GaAs NWs and the substrate used. Crystallinity and orientation of GaAs NWs were studied by X-ray diffraction (XRD) technique. Transmission electron microscopy (TEM) was used to obtained accurate information about defects and structure in GaAs NWs. Electrical conductivity of GaAs NW at different point along the NW was investigated by conductive atomic force microscopy (CAFM). With extracting data from a current-voltage measurement, the energy gap (E₀) at different section on the GaAs NW can be calculated.

1.6 Significance of the Study

Coupled with the emergence of high technology NW fabrication, semiconductor NW is produced in atomic arrangement and can be applied in the electronic and optoelectronic application. GaAs NWs due to its properties such as high electron mobility, direct band gap and high quantum efficiency are potentially use in solar cells and lasers.

On the fabrication, the vertical reactor used in this study are rarely been used by other researchers. Various parameters such as annealing temperature on gold colloids, growth temperature, growth period, V/III ratio and substrate orientation can
be modified to produce an optimum value of effective NWs. Although many studies have been done on the different growth temperature, the values that were found are different. This may depend on the characteristics of the device itself. The detailed studies of catalyst forming also are not fully explored. In this regard, studies relating the effect of annealing on gold colloids and NW formation will be discussed in detailed. Direct horizontal growth of GaAs NWs was determined by applying extended annealing process on the gold colloids. GaAs NWs have successfully been grown on different orientation substrate such as (100), (311)B and (110) with minimal twin defect structure compared to when using (111)B substrate. Another factor that influences the structure of the GaAs NW is the growth rate of NWs. Through the observation of growth rate of NWs, the activation energy of a substance and minimum diameter of GaAs NW can be calculated. This was also a significant study of GaAs NW and the Au nanoparticles catalyst.

In the structural characterisation of GaAs NWs, the equipment that is used does not only measure the micro size, but even up to atomic level resolution including FE-SEM and TEM. In electrical properties, measurements made were based on actual usage of applications in semiconductor industries. This is in contrast with the other characterisations which focused on the chemical analysis. The tool used in the characterisation of the electrical properties is conductive atomic force microscopy (CAFM). Study on the structural and electrical properties can enhance the basic understanding on the effect of those parameters on the GaAs NWs.

1.7 Outline of Thesis

Chapter 1 presents a general background of nanotechnology, semiconductor NWs and the growth review of GaAs NWs. This is followed by the objectives and scopes of the study. The general physical properties of bulk GaAs are presented in Chapter 2. Theory on vapour-liquid-solid related to the NW growth is also described. Chapter 3 focuses on the experimental works including GaAs NW growth and characterisation process. A brief overview of each characterisation technique was discussed. Results and analyses are reported in Chapter 4. This chapter is
divided into four sections referring to the four different objectives but closely related. Section One is related to optimal parameters. The effects of different growth parameters such as annealing effect on the gold colloids, growth temperature, growth period and V/III ratio are studied in order to achieve optimised growth conditions. Section Two involves the annealing process on the NW formation. Section Three is referring to different orientation substrates used to NW structure and lastly the electrical characterisation of GaAs NWs was discussed in Section Four. Chapter 5 concludes the thesis by describing the main observations and recommending some future works.
REFERENCES


