EPITAXIAL METHODS OF QUANTUM DEVICE GROWTH

Rosnita Muhammad[1], Zulkafli Othaman[1],Samsudi Sakrani[1], Yussof Wahab[2]

[1]Physics Department, Faculty of Science,
Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia
[2]Ibnu Sina Institute for Fundamental Science Studies,
Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

Corresponding email address: rosnita@utm.my

ABSTRACT

Epitaxy is an affordable method for growing high quality crystalline in quantum device applications. The fabrication of the quantum devices is an outstanding challenge in nanostructure materials science. During last few years, a lot of attention has been devoted to the growth and characterization for low dimensional semiconductor materials. In this paper, we present several epitaxy methods in recent advancement. We then briefly examine the one and only epitaxial method that we have at Ibnu Sina Institute, Universiti Teknologi Malaysia i.e MOCVD system; starting with basic chemical reaction process, gas delivery equipment, reaction chambers and safety. Growth mechanisms and criteria for growth rate are also will be discussed. Lastly, we show gallium arsenide nanowires that succesfully grown using MOCVD system.

Keywords: epitaxy, quantum device, MOCVD, nanowires.

INTRODUCTION

Quantum Device contains layers of electronic and optical materials which are only one or two atoms thick. Such layers are so thin that electrons can only move in the plane of the material. Beyond this will be strictly one-dimensional wires and even zero-dimensional dots, which would be tantamount to custom-designed atoms. Devices based on a single photon and single electron can provide a new challenging in nanotechnology today. Nanowire or quantum dot have such a smaller scale in one or zero dimensional structures that their electronic properties are significantly different compare to the same material in the bulk form. These properties are changed by quantum effects [1]. New epitaxial growth techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) are possible to produce nanowire and quantum dot in practice. In this paper, we present both the popular epitaxial techniques and then go further into MOCVD system which located at Ibnu Sina Institute. Lastly, we show some results on the gallium arsenide nanowires that successfully grown using the MOCVD reactor.

EPITAXY METHOD

The word epitaxy refers to the ordered growth of a crystalline material on top of a crystalline substrate, such that the crystal lattice of the new layer is in registration with that of the substrate (Figure 1) [2]. Epitaxial semiconductor layers are used in most

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved

semiconductor device fabrication processes because of the ability to accurately control the crystal composition and doping concentration and to form atomically abrupt hetero-interfaces. The techniques for epitaxial growth have typically been divided into processes that deliver the molecules for crystal growth in the liquid phase (LPE), in the gas phase, or processes that deliver the molecules in a vacuum chamber in molecular beams. Depending on the technique, the atoms for crystal growth arrive as elemental species or within precursor molecules that thermally or chemically decomposed on the surface to leave the desired species for epitaxy.

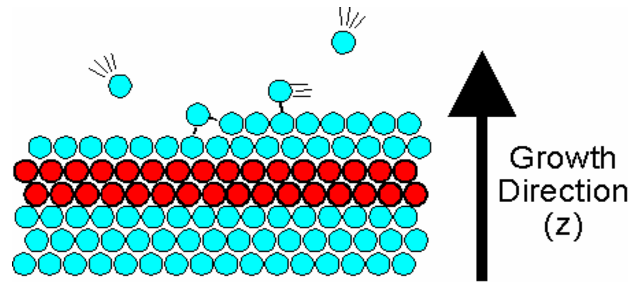

Figure 1 : The ordered epitaxial growth of a crystalline material on a substrate.

Various technique are used for growing epitaxial layer but the new crystal growth techniques have been used are molecular beam epitaxy, MBE [3-4] and metalorganic chemical vapor deposition, MOCVD [5-6]. MOCVD is also referred to, and used interchangeably with, MOVPE/OMVPE (metallorganic/organometallic vapor phase epitaxy). MOCVD is a broader term that is applicable to the deposition of crystal, polycrystalline and amorphous materials. Both MBE and MOCVD have produce a wide range of very high-purity semiconductor materials with excellent optical and electrical properties [7].

Molecular beam epitaxy (MBE)

Molecular Beam Epitaxy (MBE) is an Ultra-High-Vacuum (UHV)-based technique for producing high quality epitaxial structures with a monolayer (ML) control. Since its introduction in the 1970s as a tool for growing high-purity semiconductor films, MBE has evolved into one of the most widely used techniques for producing epitaxial layers of metals, insulators and superconductors as well, both at the research and the industrial production level. The principle underlying MBE growth is relatively simple: it consists essentially of atoms or clusters of atoms, which are produced by heating up a solid source. The clusters then migrate in an UHV environment and impinge on a hot substrate surface, where diffusion process occurred and incorporate into the growing film (Figure 2).

The growth of uniform epitaxial films from multiple effusion cells requires special effusion cell geometry and continuous rotation of the substrate around an axis normal to the substrate surface. The substrate holder can rotate with speeds up to 125 rpm. The control unit remotely orients the sample holder into any of hour positions: growth, transfer, E-beam and auxiliary [8]. The controller also allows remote to adjust the speed rotation. The modern commercial MBE growth chamber (Figure 3) is often equipped with a rotary substrate manipulator capable of turning the substrate azimuthally during

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved

growth. With this feature the substrate can be heated more uniformly and resulting the uniformity and good layers structure [9].

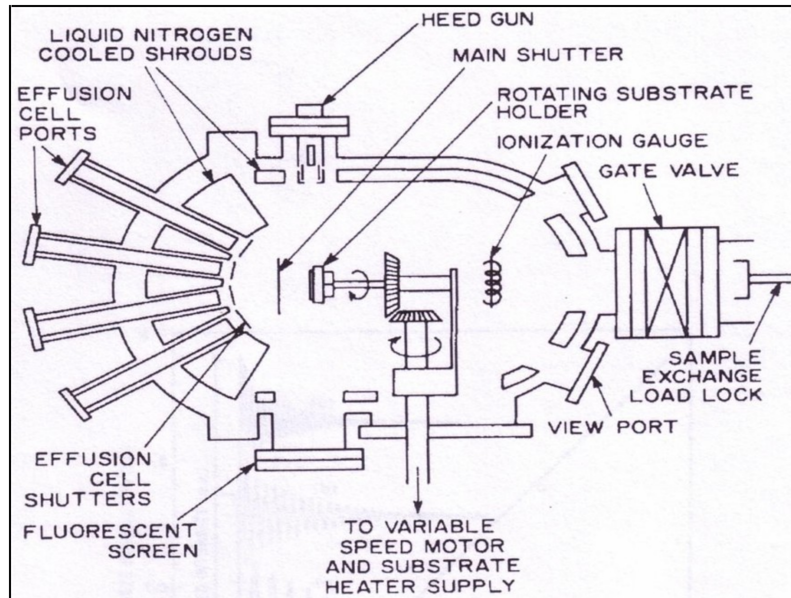

Figure 2 : MBE cut-away system viewed from the top [8]

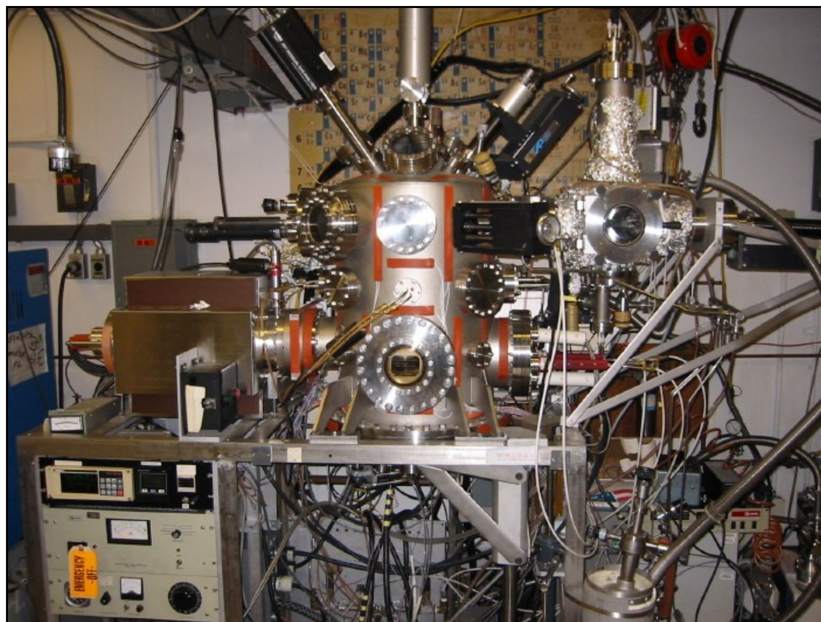

Figure 3 : MBE System at MIT, Cambridge

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved

Metal Organic Chemical Vapor Deposition (MOCVD)

MOCVD is the epitaxial crystal growth technology of choice for an impressive array of commercial devices, including lasers, light emitting diodes (LED), heterostructure bipolar transistors, photodetectors and solar cells. The growth process in MOCVD is similar to MBE, but the atoms are carried in gaseous form to the substrate (Figure 4). For example, to grow epitaxial GaAs, the gasses can be trimethyl gallium and arsine. These precursor molecules thermally decomposed on a hot substrate, the resulting organic molecules evaporate, leaving the Ga and As atoms for incorporation into the crystal. Typical growth temperatures are in the range 340 - 570°C, and the growth rates are on-the-order-of 1 molecular layer of GaAs per second. This growth rate allows the precursor gasses to be switched quickly enough to give very abrupt material interfaces. The growth process given by;

$$(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4 \quad (1)$$

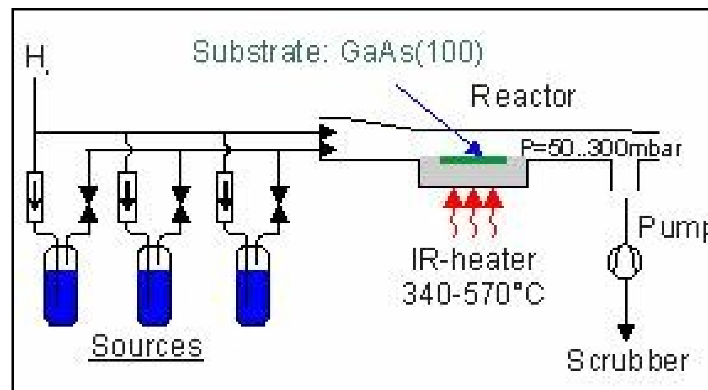

Figure 4 : Schematic view of a MOCVD reactor

The most important organometallic compounds that have been studied are trimethylgallium (TMGa), trimethylaluminium (TMAl) and trimethylindium (TMIn). These sources should be easily synthesized and easily purified related to practicalities of using several different sources together [James Coleman, 1997]. In general, the organometallic constituents are transported to the heated substrate by passing a carrier gas, usually hydrogen or nitrogen or a mixture of the two, through the compound contained in a constant-temperature bubbler vessel. Most MOCVD growth of III-V compound semiconductors and alloys involves the use of hydrides, such as arsine or phosphine, for the column V species because they are already gases and supplied from simple cylinder.

MOCVD reactors consist of three major components; the reactor gas delivery system, the reaction chamber and the reactor safety infrastructure. The reactor delivery system or gas panel is a very clean, leak-free network of stainless-steel tubing, automatic valves and electronic mass flow controllers as shown in Figure 5. Hydride delivery modules generally require a few valves and an electronic mass flow controller, since these sources are already provided as dilute, high pressure gases in gas cylinders. An important part of the main gas panel is the supply of carrier gases within a vent-run configuration.

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved

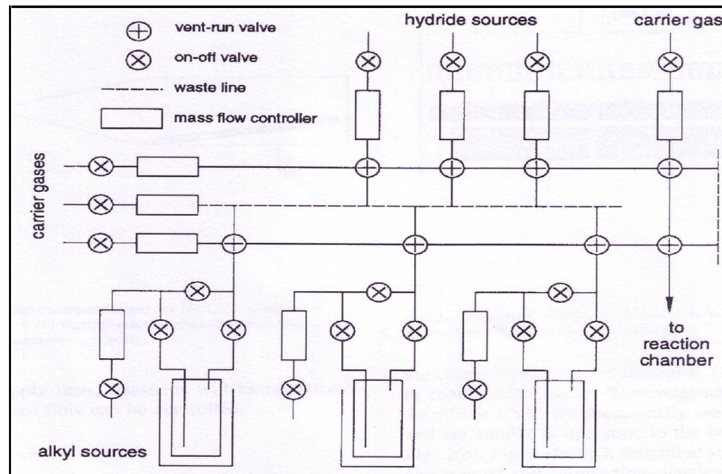

Figure 5 : Schematic diagram of MOCVD reactor delivery system gas panel, illustrating hydride delivery modules, alkyl delivery modules and the vent-run configuration.

The reaction chamber is a vessel in which the source gases are mixed, introduced into a heated zone where an appropriate substrate is located, and the basic pyrolysis reactions take place. There are two basic reaction-chamber geometries [10] commonly used for the MOCVD growth of optoelectronic materials, Figure 6. Both designs are cold-wall systems that reflect the basic pyrolysis nature of the process and make use of an indirectly heated (radio-frequency induction heated or infrared radiant heated) silicon carbide-coated graphited susceptor. The chamber itself can be quartz, stainless steel or quartz-lined stainless steel.

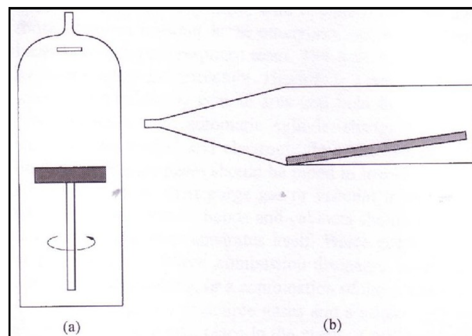

Figure 6 : Two common chamber geometry designs for MOCVD.
(a) Vertical design (b) Horizontal design

Safety is of paramount importance in the design and operation of MOCVD growth apparatus whether the sources used are hydride or not [11]. Hydrides pose the biggest risk because they are high-pressure toxic gases. The alkyls pose the next highest risk because, although they are toxic and pyrophoric, they are liquids and generally easier to handle. Ancillary risks include quartz reaction chambers (which are breakable), large volumes of explosive hydrogen gas, high temperatures, and the acids and solvents used for preparing for, and cleaning up after, a growth run. Handling these risks, falls into

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved

three categories applies equally well to all epitaxial growth process indeed to all semiconductor processing activities. The first is limited access, requires a higher level of authority and a correspondingly higher level of training. The second is training which required emergency-response situations such as hazardous-materials response and the third category is a hardware safety infrastructure. Automatic shutdown of gases source and a switch to purge inert gases should take place in the event of power failure when inadequate backup power is available.

The hydrodynamics of the reactor geometry play a key role in the nature of the process for MOCVD growth. In practical reactors, a large mismatch often exists between the inlet tube, which typically is a standard tube size of less than 10mm diameter and the characteristic dimensions of the reaction chamber. Thus, even in a relatively simple horizontal reaction chamber, the gas may have to travel well into the chamber before a simple parabolic profile stabilizes. A heated zone is necessary to drive the pyrolysis reaction and provide for the desired materials deposition. The temperature gradient between the susceptor and the chamber ambient can be very large, often several hundreds of degrees Celsius. For example, the optimum MOCVD growth temperature for many III-V compunds and alloys falls in the range of 600-800°C. Air or water cooling is often used to maintain the chamber walls at temperature close to room temperature.

MOCVD at Ibnu Sina Institute (IIS), UTM

Ibnu Sina Institute, UTM gearing up the research by moving forward on state-of the-art equipment on MOCVD system and since now, it was the first IPTA's in Malaysia which well equipped with MOCVD system. The system has been installed on Feb 2007 and the hands on training a week after. Figure 7 shows the author operated the MOCVD system which located at Ibnu Sina Institute Cleanroom.

Figure 7: The author with the MOCVD system at IIS, UTM. Picture on the right side is the vertical chamber which the sources gas mixed to produce epitaxial layer (in front of the author).

Constant source delivery is critical for thin quantum well optoelectronic devices and will have implications in the growth of thicker heterostructures in materials system that must be lattice matched. Small changes in a flow carrier gas can significantly change the source delivery. Therefore, the design of gas delivery systems must avoid transients from switching or dead space (Figure 8). The reactor delivery system must be very clean, leak free, stainless-steel tubing and automatic valves.

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved

Figure 8 : MOCVD reactor delivery system with manifold gas panel.

RESULTS AND DISCUSSIONS

One of the successfully results growth using our MOCVD reactor was the growth of gallium arsenide (GaAs) nanowire on GaAs substrate using vapor-liquid solid (VLS) mechanism. By this technique, free-standing crystalline nanowires of semiconductor with fully control nucleation sites and diameter from pre-formed metal catalyst can be grown. The growth of GaAs nanowire on GaAs substrate at 420°C was carried out using trimethylgallium (TMGa) and 10% Arsine. The sources were carried out by purity hydrogen gases throughout the palladium purifier. Figure 9 shows the MOCVD process flow of GaAs nanowire. Basically, it contains 4 different steps. The first step is susceptor bake which is done at lower temperature, usually at 200°C for 3 min. The second step is colloidal gold annealing process. This process is priority for the formation of eutectic temperature alloy between Ga and gold and during this step, AsH_3 gas overpressure supplied. The next step is the GaAs nanowire growth. Before the TMGa and AsH3 sources inject to the chamber, the flow source of the trimethyl gases need to stabilize in the line usually for 5 min. The gas source supply rates for TMGa and AsH3 were at 1.0 and 25 sccm respectively. The last step is cooling down the substrate to zero degree or room temperature with AsH_3 flow overpressure supplied for 10 min to the substrate surface.

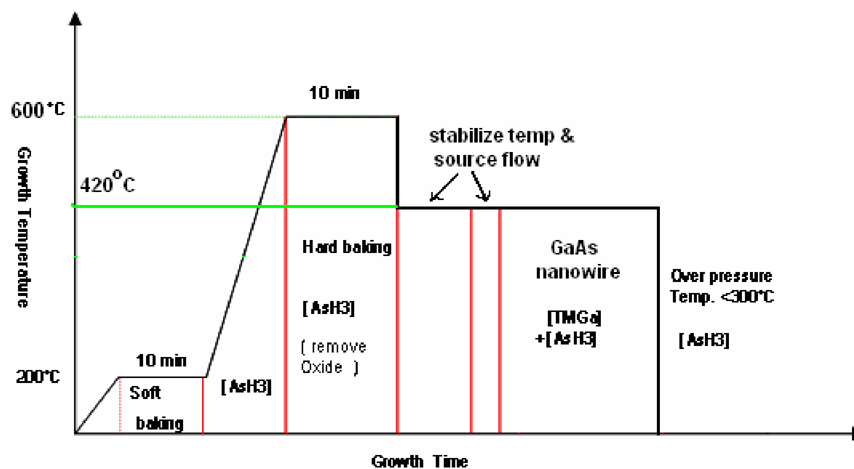

Figure 9 : MOCVD flow process of GaAs nanowire

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved

The GaAs nanowires was observed using Transmission Electron Microscopy (TEM) for crystal structure characterization. GaAs nanowires firstly, were broken off from the substrate surface by putting a specimen in a vial bottle contained acetone and sonicated for 20 min. A small (~5µl) of the solution was then pipette onto a standard TEM copper carbon holey grid. The result was shown in Figure 10. The nanowire was of zinc blende structure. The inset shows a high-resolution TEM image of the wire with highly epitaxial layers grown by layered in periodic scale and less defect formed. The measured lattice spacing perpendicular to the nanowire axis (indicate by arrow) is 0.328 nm, consistent with the (111) planar spacing of 0.326 nm for bulk GaAs [12].

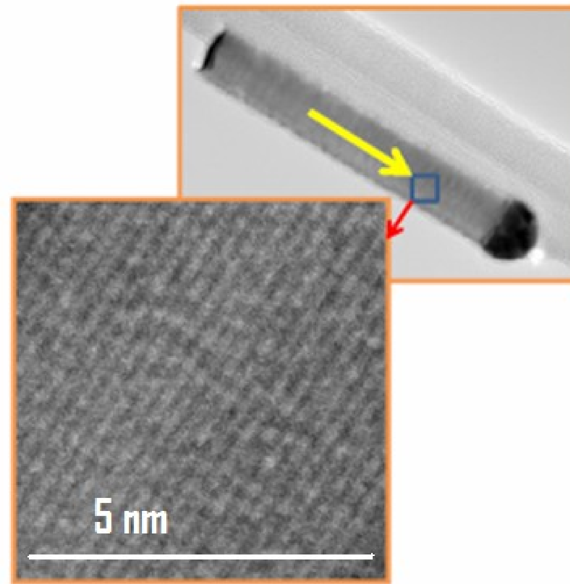

Figure 10 : Transmission Electron Microscopy image of GaAs nanowire grown at 420°C

SUMMARY

We have attempted to capture the essence of the epitaxial methods for quantum devices growth by focusing on MBE and MOCVD. We describe and examine deeper on MOCVD by considering basic chemical reactions, the TMGa and TMIn metal organic sources, the safety and the chamber reactor where the chemical reaction takes place. It is worth adding a few words to address the competition between MOCVD and MBE which are fundamentally very different. The first is that, in the hands of experts, both processes can produce similar results, and the limitations are generally those fundamental to the materials chosen rather the utilized process. The second is that, the development of each process has been accelerated by advances in the other, to the point where both processes, as well as the technical community in general, are the better for the competition.

ACKNOWLEDGEMENTS

The authors acknowledge the Ministry of Science, Technology and Environment Malaysia for the financial support through IRPA funding 09-02-06-0156-SR0013/06-01.

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved

Besides, the authors also acknowledge the Ibnu Sina Institute for lab facilities especially MOCVD system.

REFERENCES

1. Henini, M. Self-Assembled QDs for Optoelectronic Devices: Progress and Challenges. *Research on Integrated Quantum Electronics*. 2004. 3: 97 – 110.
2. Eric Donkor. GaAs-Based Nanodevices. *Encyclopedia of Nanoscience and Nanotechnology*. 2004. 3: 703-717.
3. Liang, B. L. Wang, Z. M. Mazur, Y. I. Strelchuck, V. V. Holmes, K. Lee, J. H. Salamo, G. J. InGaAs Quantum Dots Grown on B-type High Index GaAs Substrates: Surface Morphologies and Optical Properties. *Nanotechnology*. 2006. 17 (11): 2736-2740.
4. Der-Cherng Liu, Chien-Ping Lee and Shyi-Long Shy. Fabrication of Quantum Dots Using In-situ Etching and Regrowth During MBE Growth. *Electron Devices Meeting*. 1993: 427-429
5. Krost, A., Heinrichsdorff, F., Bimberg, D., Bläsing, J., Darhuber, A. and Bauer, G. X-Ray Analysis of Self-Organized InAs/InGaAs Quantum Dot Structure. *Cryst. Res. Technology*. 1999. 34(1): 89-102.
6. James J. Coleman. MOCVD for Optoelectronic Devices. *Proc. of The IEEE.* November 1997. 85(11): 1715-1730.
7. Arakawa, Y. Fabrication of Self-Assembling QDs for Photonic Devices Appl. *Proc. of the 1st Symposium on Atomic Scale Surface and Interface Dynamics*. March 13-14, 1997.
8. Chang, C. Y. and Francis Kai. *GaAs High-Speed Devices*. John Wiley & Sons. 1994.
9. Lee, S. C., Dawson, L. R. and Brueck, S.R. J. *Appl. Phys. Lett.* 2005. 87, 071110.
10. Manasevit, H. M. Single-crystal Gallium Arsenide on Insulating Substrates. *Appl. Phys. Lett.* 1968. 12(4): 156-159.
11. Johnson, E., Tsui, R., Convey, D., Mellen, N. and Curless, J. A MOCVD Reactor Safety System for a Production Environment. *Journal of Crystal Growth*. 1984. 68(1): 497-501.
12. Wu, Z. H., Mei, X., Kim, D., Blumin, M., Ruda, H. E., Liu, J. Q., Kavanagh, K. L. Growth, Branching and Kinking of Molecular-Beam Epitaxial <110> GaAs Nanowires. *Appl. Phys. Lett.* 2003. 83:3368.
13. Hiruma, K., Yazawa, M., Katsuyama, T., Ogawa, K., Haraguchi, K., Koguchi, M. and Kakibayashi, H. Growth and Optical Properties of Nanometer-scale GaAs and InAs Whiskers. *J. Appl. Phys.* 1995. 77: 447-462.

0128-8644/2009 – Jabatan Fizik UTM. All rights reserved