The Final Report

Title: Molecular Beam Epitaxy on Aligned Carbon Nanotube Arrays for Nanoelectronic Applications

Principal Investigator:
Jong Chun Woo, Ph.D., Professor
School of Physics
Seoul National University
Shinlim-Dong 56-1, Kwanack-ku
Seoul 151-747 South Korea
Telephone: +82-2-880-6597
Facsimile: +82-2-871-7507
E-mail: jcwoo@snu.ac.kr
jcwhello@yahoo.com

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14. ABSTRACT

The result on molecular beam epitaxy of GaAs and AlGaAs using carbon nanotubes (CNTs) as a crystalline seed is reported. At the growth temperature TG ≥ 600 oC, GaAs wraps around CNTs forming wirelike configuration, while Al composites form dot-like formation. At TG < 550 oC, both GaAs and AlGaAs form dot-like droplets along CNTs. Raman and XRD show the dots and wires of III-arsenide on CNTs have well-defined crystalline structure. And, the results also are indicative that tangential phonon mode and inter-atomic spacing of CNTs are affected by the interfacing of CNTs and III-V?s.

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Hybridization of GaAs, AlAs and (Al, Ga)As with carbon nanotubes by molecular beam epitaxy

I. T. Jeong[1], **M. B. Lee**[1], **J. Im**[1], **S. Hong**[1], **J. Park**[2], **M. J. Seong**[2], **S. J. Rhee**[3], **D. H. Woo**[4], and **J. C. Woo**[*1]

[1] School of Physics, Seoul National University, Seoul 151-747, Korea
[2] Department of Physics, Chung-Ang University, Hukseok-dong, Dongjak-ku, Seoul 156-756, Korea
[3] Department of Physics, Hankuk University of Foreign Studies, Yonginsi, Kyunggi-do 449-791, Korea
[4] Korea Institute of Science and Technology, Seoul 136-791, Korea

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The result on molecular beam epitaxy of GaAs and AlGaAs using carbon nanotubes (CNTs) as a crystalline seed is reported. At the growth temperature $T_G \geq 600$ °C, GaAs wraps around CNTs forming wire-like configuration, while Al composites form dot-like formation. At $T_G < 550$ °C, both GaAs and AlGaAs form dot-like droplets along CNTs. Raman and XRD show the dots and wires of III-arsenide on CNTs have well-defined crystalline structure. And, the results also are indicative that tangential phonon mode and inter-atomic spacing of CNTs are affected by the interfacing of CNTs and III-V's.

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1 Introductory remarks In recent years, one-dimensional (1-D) and zero-dimensional (0-D) semiconductor structures have been attracting a tremendous attention due to their exotic electronic and optical properties. One of the outstanding examples in 1-D nanostructure is carbon nanotubes (CNTs) and nanowires [1], but they impose the limit in application due to its physical properties. On the other hand, in spite of numerous ingenious efforts, the fabrication of 1-D and 0-D structures with III-V semiconductors still has room for improvement in controllability of their size and site. The primary objective of this work is to integrate the merits of CNTs and III-V compound semiconductors with the aim of using III-V compound semiconductor as active material in electronic and optoelectronic devices. The hybridization of CNTs and III-V compound semiconductors such as GaAs, AlAs and InAs forming dots and wires would bring a new scope of nanoelectric devices, if we could highlight the merits of these materials. Few efforts of these kinds have so far been reported, except CNTs encapsulated in GaMnAs functioning as the one-dimensional active transporting channel [2, 3].

In this paper, the molecular beam epitaxial (MBE) growth of GaAs and AlGaAs nanostructures deposited on CNTs is reported with the analytical results of their crystalline and structural formation through atomic force microscopy (AFM), Raman spectroscopy and X-ray diffraction (XRD).

2 Preparation of CNTs and III-V MBE growth Five kinds of surfaces, GaAs, $Al_{0.5}Ga_{0.5}As$, AlAs, Si and SiO_2, are used as substrate for CNT deposition, and consequently as substrate in MBE growth. Single-walled carbon nanotubes (swCNTs) prepared via the HiPCO method are dispersed in 1,2-dichlorobenzene without using any surfactant to prepare pristine swCNT suspensions with a concentration of ~0.2 mg/ml [4]. The deposition of uniform layer of swCNTs on various substrates was achieved

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[*] Corresponding author: e-mail: jcwoo@snu.ac.kr, Phone: +82 2 880 6597, Fax: +82 2 871 7507

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by dipping the substrates in the swCNT suspensions until it reaches the desired surface coverage. A relatively high coverage of swCNTs was achieved by directly dropping suspensions of swCNTs onto the substrates and drying the solvent. Even though we were able to direct the swCNT assembly using various organic monolayer patterns [4], organic molecules are not utilized in this experiment to minimize possible contamination. The quality and coverage of the prepared swCNT layers are checked via the AFM method.

The growth conditions of GaAs and (Al,Ga)As epitaxial layers in the MBE system are set by changing the growth temperatures (T_G) from 350 °C to 650 °C in step of 50 °C, except an additional step of 620 °C in AlGaAs with epitaxial layer growth of 2 minutes which would give approximately 5 nm epitaxial thickness, if covered uniformly on GaAs substrates. Before the growth, substrates covered with CNTs are treated thermally at 450 °C at 10^{-10} Torr for 10 minutes and again at 600 °C under As-rich 10^{-10} Torr background for 5 minutes. A typical growth rate of GaAs epilayer is 1 µm/hr, and the background pressure of the growth chamber before the growth is typically 2~3x10^{-11} Torr. With the established growth conditions, various GaAs/AlGaAs structures have been attempted.

3 AFM topography Typical AFM topography images of MBE-grown GaAs and AlAs on CNTs are shown in Fig. 1. All of these specimens have 2 minutes epitaxy time and AlGaAs substrates. The image of GaAs grown at T_G = 600 °C shows that GaAs aligns along CNTs, forming ‘wire-like’ configuration, and the thickness of the wire is relatively uniform along CNTs except at the tips of CNTs or the spots where CNTs are bundled, as seen in Fig. 1(a). On the other hand, AlAs (and even AlGaAs) grown at 620 °C (even at 650 °C) forms droplets or dot-like formation, even though the deposition is favored along CNTs, as in Fig. 1(b). In Fig. 1(c) and (d), GaAs and AlAs at T_G = 450 °C are presented, which show formation of droplets along CNTs. These are typical formation at $T_G \leq$ 550 °C for both GaAs and AlAs.

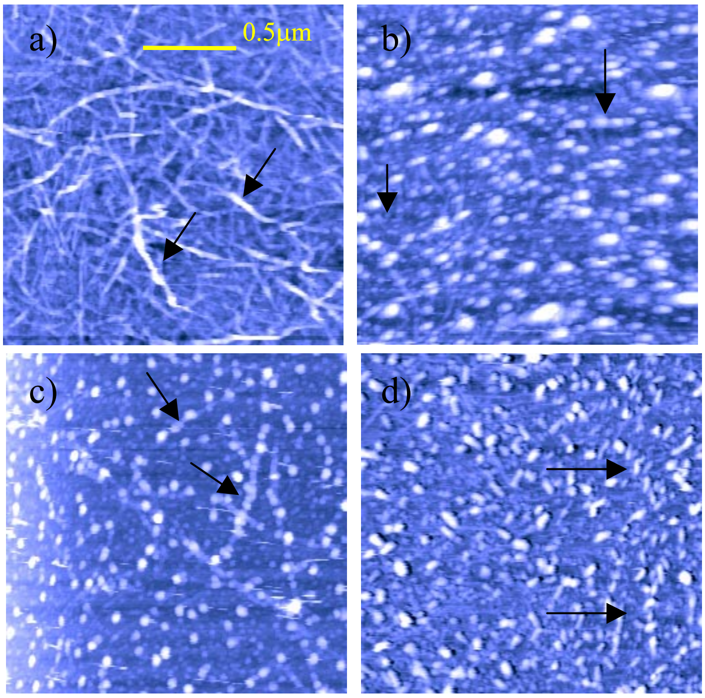

Fig. 1 AFM topography images of III-V semiconductors MBE grown on GaAs substrate, which is covered with a single layer of CNTs in random orientation. (a) GaAs grown at T_G = 600 °C, (b) AlAs at T_G =620 °C, (c) GaAs at T_G = 450 °C and (d) AlAs at T_G = 450 °C. Wire-like formation along CNTs is observed in (a), while in (b), (c) and (d) dot-like formations are detected along CNTs. Noticeable sites are indicated with arrows.

When thicker GaAs and AlGaAs epilayers are deposited, they tend to spread over the GaAs and AlGaAs substrate and progress to form flat surfaces, while CNTs remain to be the more favourable nucleation

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sites over Si and SiO_2 substrates and the clustering continues. Material of substrate influences little on nucleation and crystalline formation. Preliminary indication is tips and defects of CNTs as well as the contact points between CNTs and substrates are favorable nucleation sites. The specimens of GaAs interfaced with CNTs form 'wire-like' structure along CNTs, while the Al compound tends to form 'dot-like', indicating difference of adhesive or binding properties of Al and Ga with CNTs. This tendency is clear in the Raman analysis, as described in the next section.

4 Raman spectroscopy and XRD results The crystallization of GaAs on CNTs was examined by Raman spectroscopy and X-ray diffraction (XRD).

In Raman spectra obtained at room temperature, specimens of GaAs and GaAs/AlGaAs deposited on CNTs, the radial breathing (RB) mode and tangential vibrational mode (G-band) of CNTs are distinct at 188, 1592 cm^{-1}, respectively. GaAs LO and TO phonon modes at 291, and 269 cm^{-1}, and AlAs TO and LO at 362 and 388 cm^{-1}, respectively, for AlGaAs containing specimens, are clearly observed. This is an indication of good crystalline quality. A typical Raman spectrum is shown in Fig. 2.

It is noticed that the intensities of both RB mode and G-band of CNTs are relatively weak in the specimens of GaAs interfacing CNTs. The side peak of G-band, which is believed to originate from the coupling with III-V, is more distinct in these specimens. The XRD peak related to CNTs appearing at 50.3°, less by 2° than that of usual CNTs, is indicative contraction of tangential inter-atomic distance due to III-V deposition. These Raman and XRD results also support that CNTs interface more tightly and more widely covered with GaAs than Al composite. The material property of substrate influences little on the crystalline formation for the epilayer thickness of up to 20 nm.

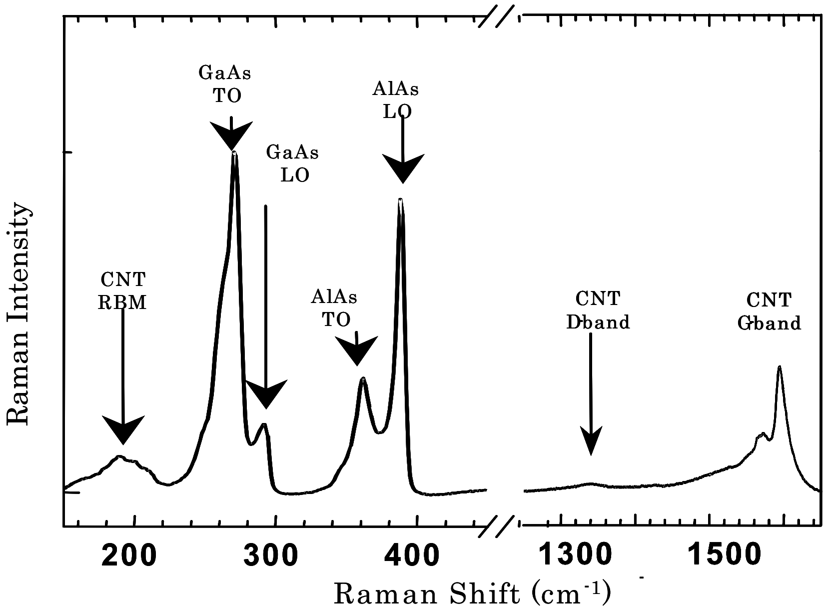

Fig. 2 A Raman obtained from specimen of GaAs/AlGaAs on CNT deposited on SiO_2 surface is shown as an example. Peaks at 188, 291, 269, 362, 388, 1335, and 1592, cm^{-1} are identified as CNT radial breathing mode, GaAs LO and TO modes, AlAs TO and LO modes, CNT defect band and CNT G-band (tangential modes), respectively.

Nucleation behaviour on CNTs in MBE growth of GaAs related material becomes clear from Raman on Si substrate. Si substrates with CNTs present distinct and intense Raman signals of GaAs and AlAs with no distinguishable Si-related peak. But, GaAs grown on Si-substrate with no CNT deposition has dominant Si peak at 512 cm^{-1} and almost indistinguishable GaAs and AlAs peaks. This result unambiguously demonstrates that CNTs play a significant role in nucleating quality GaAs structures. The similar effect of CNTs is also observed at GaAs-related III-V growth on SiO_2/Si substrates.

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The glanced angle XRD (incident angle of 0.05°) data show distinct and sharp peaks corresponding (111), (220) and (311) of GaAs (thus also AlGaAs), as seen in Fig. 3. Also observed is CNT peak at 50.3°. The peak at 27.6 ° is superposition of with GaAs (111) and CNTs. This result also confirms the crystalline formation of III-V materials on CNT-covered substrates.

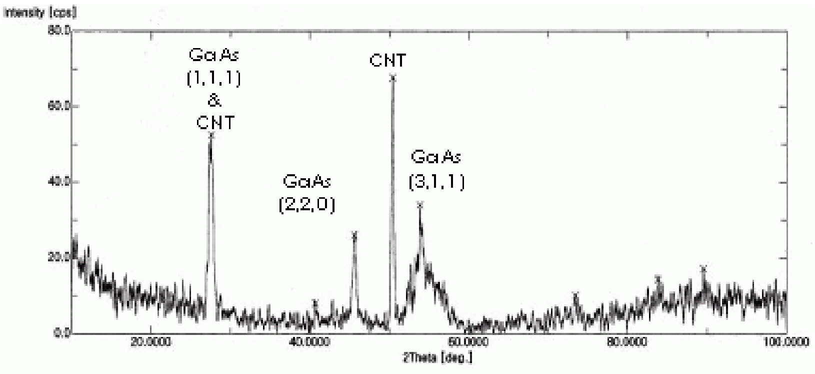

Fig. 3 Small incident angle XRD data obtained from the specimen of GaAs/AlGaAs on CNTs (deposited on SiO_2 surfaces). The peak at 27.6° is identified as superposition of GaAs (111) and CNTs. Those at 45.6°, 50.3°, and 53.9° are GaAs (220), CNT and GaAs (311), respectively.

5 Conclusive remarks The result shows that CNTs are outstanding crystalline nucleation for GaAs and AlGaAs. It also shows that GaAs interfacing with CNTs forms wire along CNTs at $T_G \geq 600$ °C and dot at $T_G \leq 550$ °C, while AlGaAs forms dot at any $T_G \leq 650$ °C of our attempt. Even though AlGaAs by itself would form dots, a thin wetting layer of GaAs leads AlGaAs to form wire on top of GaAs. These epitaxial characteristics provide us means of controlling GaAs and AlGaAs crystalline formations to become wire or dot in the self-assembling deposition process, when hybrided with CNTs. Furthermore, it also implies that when CNTs aligned in patterned configurations [4] are used as a nucleation, we could obtain III-V quantum dots and quantum wires aligned with regularity and of reasonable uniformity in their physical dimensions.

This uncharted hybridization of GaAs related compound and carbon nanostructures opens up numerous potential applications via aligned growth of nano-wire and quantum dot. While metallic CNTs could be utilized as a current lead, quantum dot or wire devices such as high-speed high mobility devices, light emitting devices and even spin-polarized devices, could be candidates in the application.

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Supplementary Results

<Note>

After publishing the results based on the crystallographic study on Physica Status Solidii, the work had been continued and the additional up-to-date preliminary results are described here.

<Additional Results>

1) Photoluminescence results at room temperature and 10 K
(Shown in Fig. 1.)

(a) Low Temperature PL

- Peak at 1.72~1.80 eV region originated from groups of the low-dimensionally (low-D) confined quantum structures
- Peak at 1.52 eV region originated from GaAs layers deposited on the substrate
- PL from low-D structures is more intense than GaAs PL

(b) Room Temperature PL

- Peak at 1.67~1.76 eV region originated from groups of the low-D confined quantum structures
- Peak at 1.43 eV region originated from GaAs layers deposited on the substrate
- PL from low-D structures is weaker than GaAs PL

2) Cathode luminescence analysis at room temperature
(Shown in Fig. 2)

- Several sharp peaks at 1.66~1.76 eV region originated from groups of the low-dimensionally confined quantum structures
- Peak at 1.43 eV region originated from GaAs layers deposited on the substrate
- Sharp peaks at 1.66~1.76 eV region are indicative of the presence of low-D confined structures of various confinement lengths.

3) Preliminary Analysis of Low-D confined structure based on Low-T PL analysis--
PL at 1.72~1.80 eV

- Comparison with GaAs/$Al_{0.5}Ga_{0.5}As$ Quantum Well: corresponds to the well width of 3~4 nm or 10~14 monolayer. (EFA calculation)
- Comparison with GaAs/$Al_{0.5}Ga_{0.5}As$ Quantum Wire: corresponds to the wire diameter of larger than 20 nm or 70 monolayer (Comparison with QWR array data)
- Therefore, our preliminary conclusion is on the configuration of the low-D structure is a tube shape, forming quantum tube as shown in Fig. 3.

<Follow-up studies in progress>

◊ CL microscopic mapping

◊ PL and CL analysis of quantum tube of various confined length

◊ Numerical modeling of ground-state subband energy of quantum tube

Fig. 1: PL Spectra at room temperature (RT) and 10 K (LT)

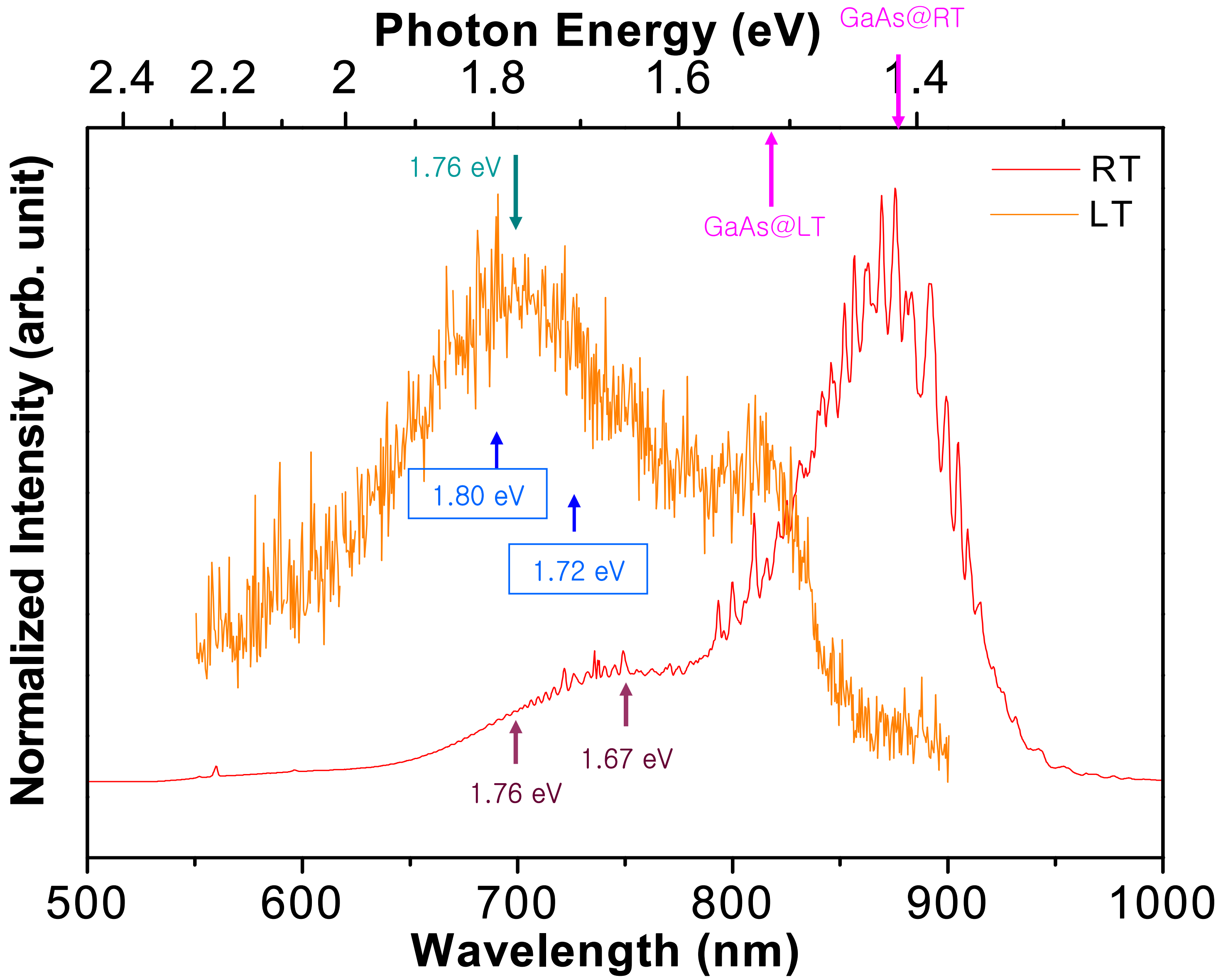
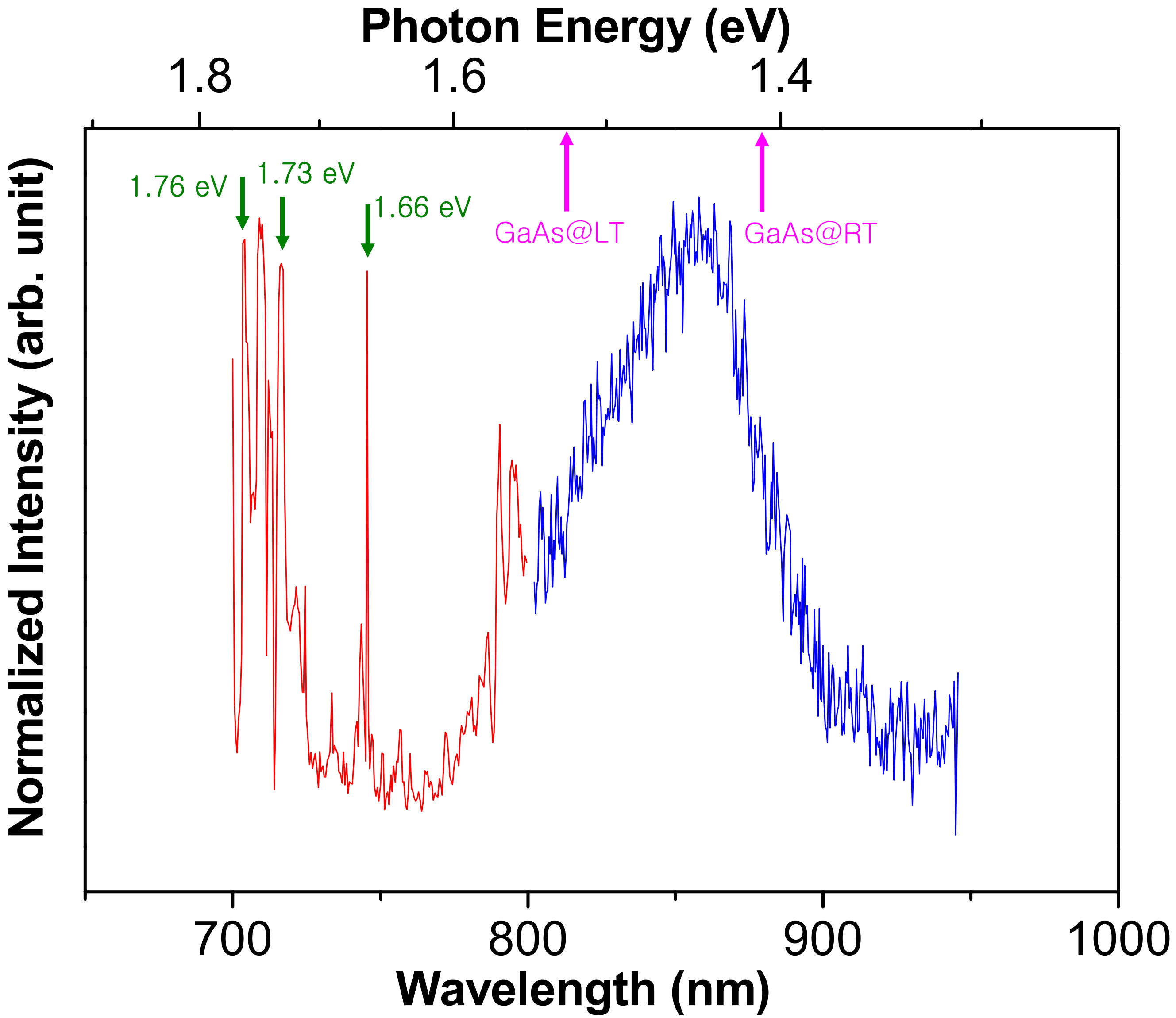


Fig.2 : EL Spectrum at room (RT) temp.



Configuration estimated from PL and CL results

- GaAs confined by AlGaAs barrier
- Nanostructures in 1-D confinement

PL Peak at 1.72~1.80 eV at 10 K

≈ GaAs/$Al_{0.5}Ga_{0.5}As$ QW of L_Z=3~4 nm

≈ GaAs/$Al_{0.5}Ga_{0.5}As$ QWR of L_W &L_Z =15~20 nm

Quantum Tube !!

- Wall thickness : approximately 4~6 nm
- Tube diameter : estimated to be 60 nm
- Length : long enough

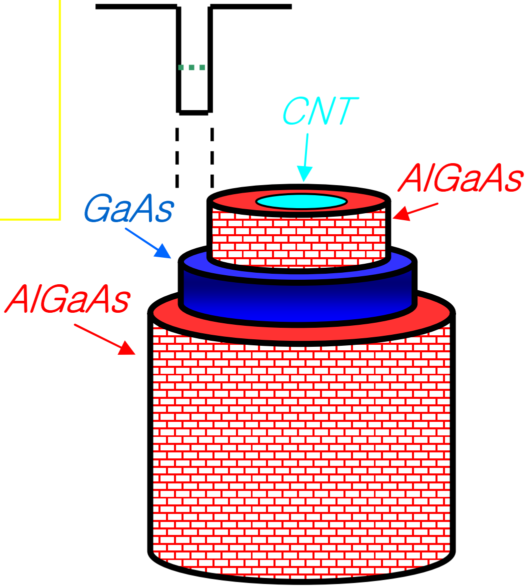


Fig. 3: Schematic diagram of the sample