Chapter 2

Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is a versatile technique for growing thin epitaxial structures made of semiconductors, metals or insulators. Many materials have been crystallized as epitaxial thin films by MBE, but semiconductors of the III-V group in general GaAs and $Al_xGa_{1-x}As$ in particular received most attention. The basic process for MBE growth of III-V semiconductors consists of a co-evaporation of the constituent elements (Al, Ga, In, As, P, Sb) of the epitaxial layer and of dopants (mainly Be for p-type and Si for n-type doping for GaAs system) onto a heated crystalline substrate where they react chemically under ultrahigh vacuum (UHV) conditions. The composition of the grown epilayer and its doping level depend on the relative arrival rates of the constituent elements and dopants, which in turn depend on the evaporation rates of the appropriate sources.

Molecular-beam apparatus was first successfully used by Cho and Arthur in the late 1960s to crystallize and investigate GaAs epilayers. High vacuum epitaxial growth techniques using particle beams have developed rapidly. This development accelerated when semiconductor devices with quantum-well structures were invented in the 1970s. It is about the same time as Esaki and Tsu predicted the intriguing properties of semiconductor superlatices, a new thin film growth technique to grow ultrathin layers and periodic multilayer structures of III-V semiconductors in reproducible is needed.

2.1 MBE System

The MBE system consists of four UHV building blocks, i.e. the load-lock chamber, the sample preparation chamber, the transfer chamber, and the growth chamber, which are separately pumped and interconnected via large-diameter channels and isolation valves. High-quality layered semiconductor structures require a background vacuum in the low 10^{-11} Torr range to avoid incorporation of background impurities into the growing layers. Figure 2.1 shows a schematic of the MBE basic system (RIBER model 32 P).

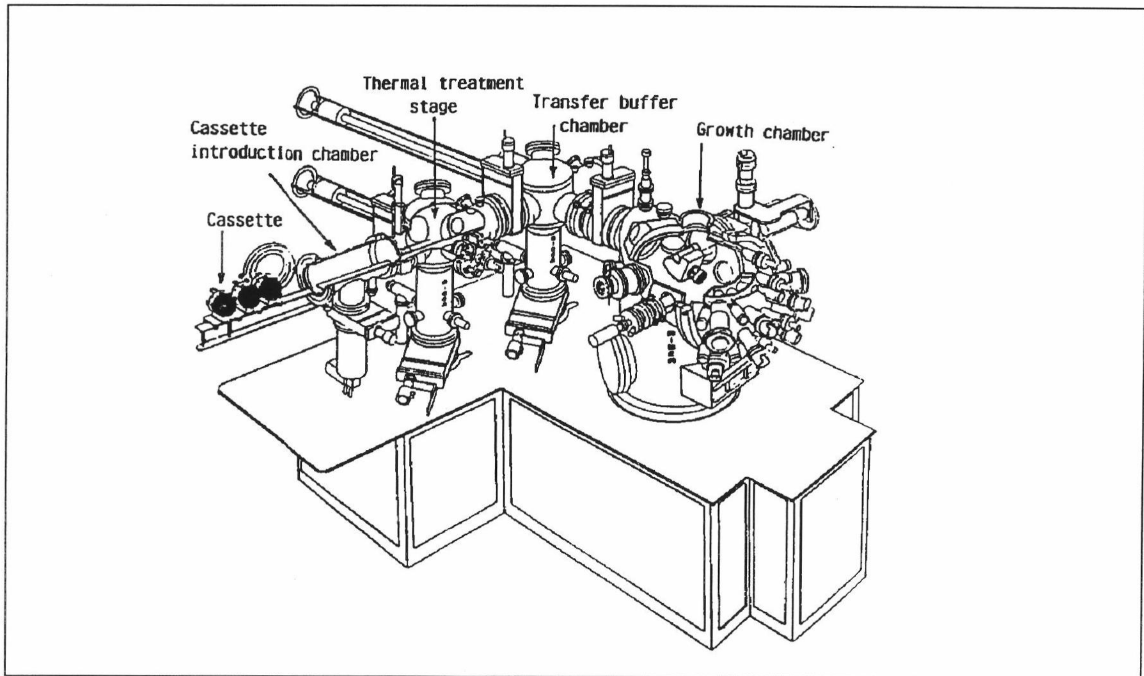

Figure 2.1 Schematic illustration of the RIBER 32 P MBE system.

The load-lock chamber is the first pre-vacuum stage to load the substrates into the MBE system, and also re-load the grown samples out. In loading procedure, the substrates which mounted on the molibdinum block are install on the trolley that can be travel pass to the other chambers through the vacuum gate valves. Before pass the samples to the next chamber called preparation chamber, the load-lock chamber must be evacuated until at lease 10^{-6} Torr.

The next adjacent chamber is the stage that the substrates must be heated (typically for GaAs substrate around 400 °C) to outgas contamination and moisture that attach on the substrate. This station has an oven that can be heat up and cool down by using computerized temperature controller.

All of the substrates that have been treated from the preparation chamber should be held in the next chamber, called transfer chamber. This chamber is used to store fresh substrates before loading into growth chamber and grown samples that are already grown from the growth chamber.

The growth chamber is the heart of the MBE system. This chamber is installed with effusion cells that contain sources to evaporate. In front of each cell has shutter to switch the evaporation beam on or off. The block which holding the substrate is place onto the manipulator and face to the center of the combine evaporation beams. In front of the manipulator placed also a main shutter to protect the substrate surface from deposition. Figure 2.2 shows a diagram of the growth chamber and illustrates *in-situ* diagnostic equipment that will be described later.

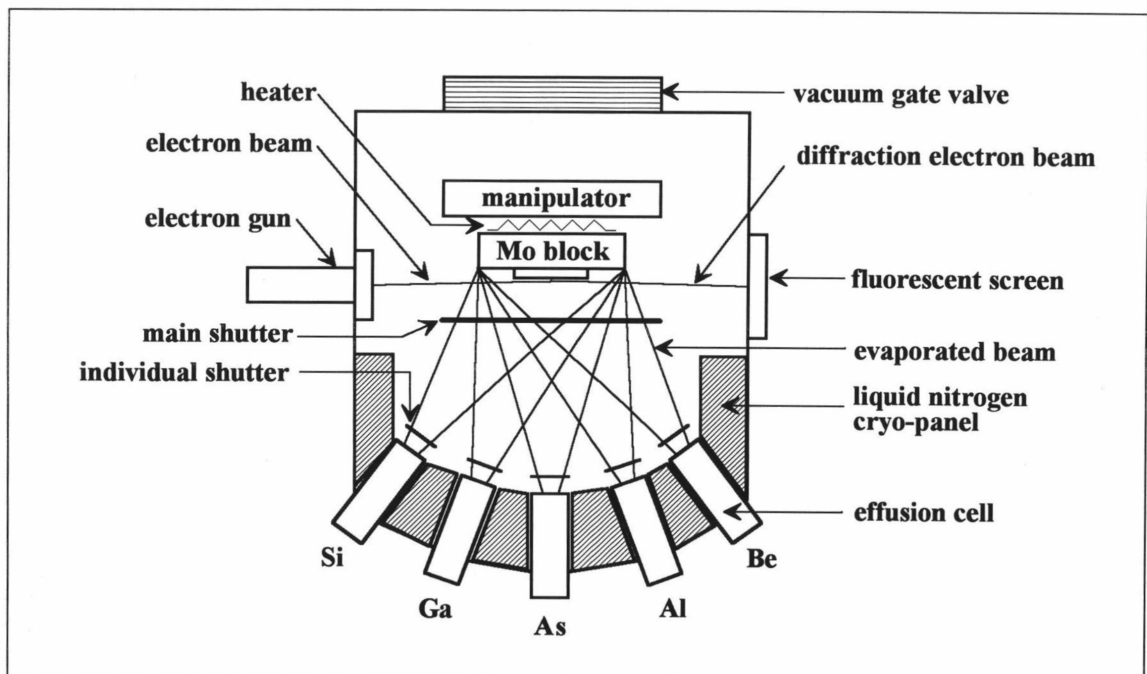

Figure 2.2 Diagram of the MBE growth chamber.

The chamber wall and the effusion cells are cooled with liquid nitrogen to prevent the contamination outgasing from the heating parts. Vacuum condition in this stage is importance to the epitaxial growth process.

The materials for the growth of III-V semiconductors are evaporated in resistively-heated effusion cells made of pyrolytic BN which operate at temperature up to 1400°C. Most of the functions important for the MBE growth process, i.e. cells and substrate temperature, shutter timing schedules, are controlled by a computer.

The intensities of the beams incident on the heated substrate crystal are controlled by the temperatures of the individual effusion cells. For typical growth rate of ~1 μm/hr, the fluxes required on the growing surface are approximately 10^{14} - 10^{15} atoms/cm^2·s for the group III elements, 10^{15} - 10^{16} atoms/cm^2·s for group V elements, and 10^7 - 10^{12} atoms/cm^2·s for the dopants. Continuous changes in the chemical composition of the growing film are achieved by programmed variation of the cell temperatures. Abrupt changes are obtained by using the mechanical shutters placed individually in front of cell orifice. The group III element beam is always atomic, while the beam of group V element can be tetratomic when generated from the elemental source or diatomic when generated by incongruent evaporation of the III-V compound itself or by using a secondary state heater as a "cracker" for tetratomic molecular beam cracking.

Figure 2.3 is a RIBER 32P MBE system which install at Semiconductor Device Research Laboratory (SDRL), Faculty of Engineering, Chulalongkorn university. This is the first MBE system in Thailand donated from JICA in 1992. The system is set for growing GaAs and relate III-V compound group such as AlGaAs, InGaAs.

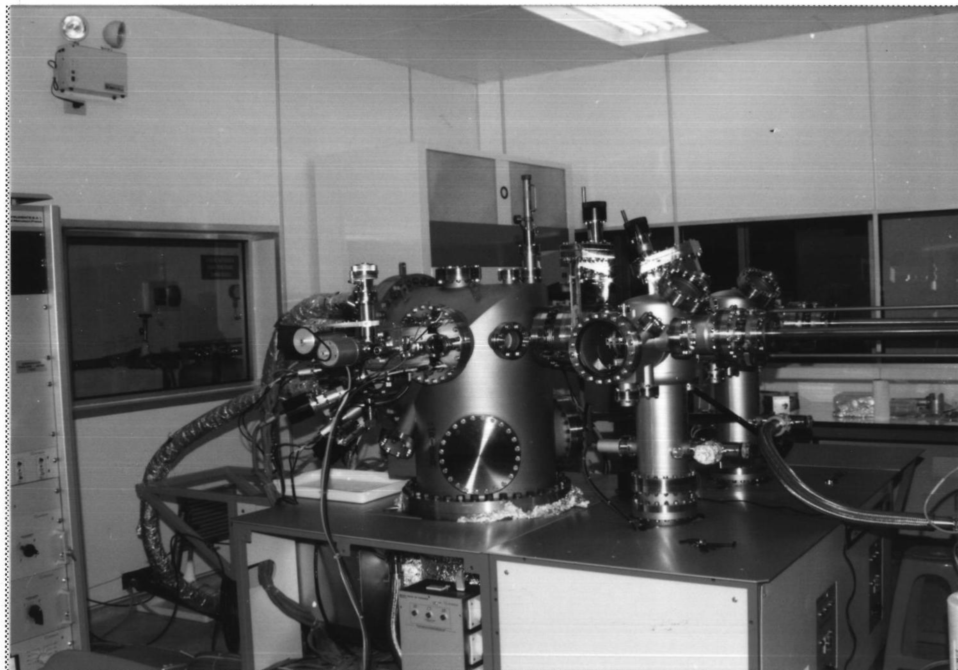

Figure 2.3 The first MBE system in Thailand installed at SDRL Chulalongkorn university.

2.2 Fundamental of The MBE Growth

If we consider the growth of GaAs on GaAs (100) surfaces from beams of Ga and As_n (n = 2 or 4) as the archetypal system, two apparently separate and identifiable processes are involved : the reaction between Ga and As_n and the surface migration of adsorbed species to correct sites in the growing lattice [5]. Figure 2.4 demonstrates how these process occur on the substrate surface.

The MBE system which has only normal effusion cell for arsenic, the growth process is from tetrametric arsenic and gallium, As_4 molecules are adsorbed into a mobile precursor state and the Ga adatom population, have a sticking coefficient equal to zero, but a measurable surface lifetime, controls the condensation and reaction of As_4. The crucial result reported somewhere is that sticking coefficient of this system can never exceed 0.5, even when the GaAs surface is covered by a monolayer of Ga atoms. For practical film growth the important result from the kinetic studies is that stoichiometric GaAs can be grown for a whole range of substrate temperatures and relative flux ratios of As_4 and Ga larger than or equal to 0.5. As a rough guideline, the GaAs films grow with an As-stabilized (2x4) surface structure when As_4/Ga flux ratio greater than 2 and the Ga-stabilized (4x2) surface structure is observed when As_4/Ga flux ratio less than 0.5.

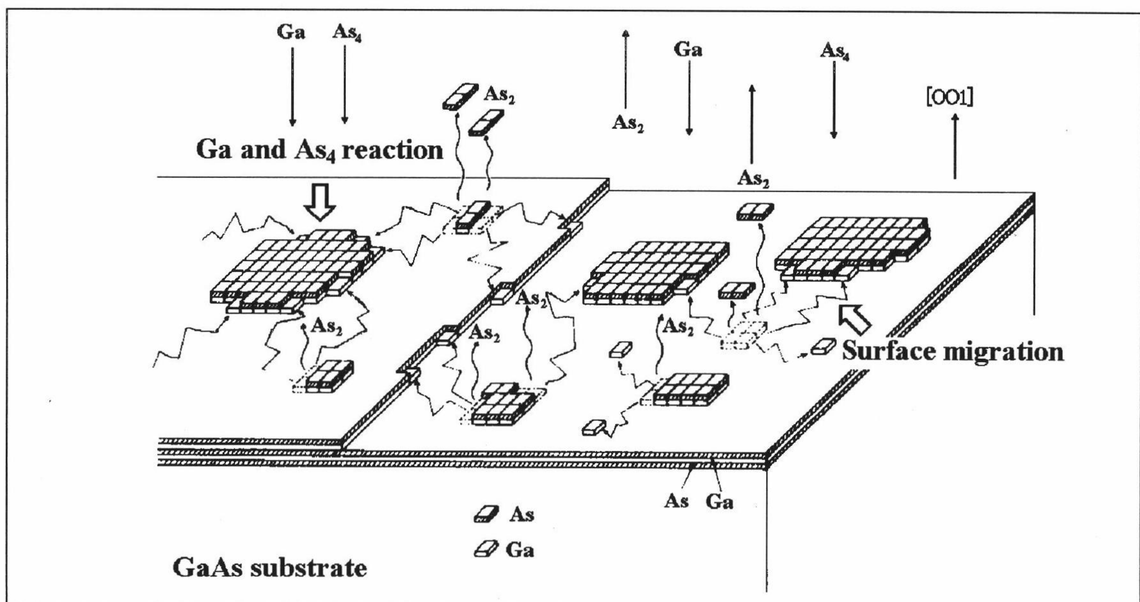

Figure 2.4 Model illustrates of the Ga and As_4 reaction and surface migration processes occur on (100) GaAs substrate surface.

The growth rate R (μm/hr) of MBE GaAs films is entirely controlled by the flux density of Ga beam F (atoms/cm^2·s) impinging on the substrate surface. The relation of $R = S_{Ga} F$, where S_{Ga} is the sticking coefficient of Ga and has a value close to unity at typical MBE growth temperatures (450-620°C) under As-stabilized growth conditions. This implies that nearly all the Ga atoms incident on the surface are incorporated into the growing epitaxial layer. It should be noticed, however, that these Ga atoms, after being adsorbed on the substrate surface, still undergo a considerable amount of migration and rearrangement.

The growth model established from kinetic measurements is not unique to GaAs. It is also valid for a number of other III-V compounds such as AlAs and InP. And with minor modifications for the ternary III-III-V alloys such as $Al_xGa_{1-x}As$. In practical terms, a good compositional control of the growing alloy film can be achieved by supplying excess group V species and adjusting the flux densities of the impinging group III beams. The principal limitation to the growth of III-III-V alloys by MBE is the thermal stability of the less stable of the two III-V compounds of which the alloy may be considered to be composed. At higher temperatures preferential desorption of the more volatile group III element occurs. Thus, the surface composition of the alloy reflects the relative flux ratio of the group III elements only [6].

The purity of most III-V semiconductors grown by MBE is limited by background impurities originating from the UHV system and from the source materials. Not intentionally doped GaAs layers with residual impurity concentrations in the low 10^{13} cm^{-3} range are now routinely achieved. The most common dopants used during MBE growth are Be for p-type and Si for n-type doping. The group II element Be behaves as an almost ideal shallow acceptor in many MBE grown III-V semiconductors. Each incident Be atom produces one ionized impurity species, providing an acceptor level 29 meV above the valence band edge in GaAs. The group IV element Si is primarily incorporated on group III sites during MBE growth under As-stabilized conditions, yielding n-type material of fairly low compensation. It is noteworthy that the incorporation of Si atoms on either Ga or As sites during MBE growth depends strongly on the orientation of the GaAs substrate. In GaAs deposited on (111)A, (211)A and (311)A orientations the Si atoms predominantly occupy As sites and act as acceptors, whereas they occupy Ga sites and act as donors on (001), (111)B, (211)B, (311)B, (511)A, (511)B and higher-index orientations.

2.3 Reflection High-Energy Electron Diffraction

An inherent advantage of MBE which is lacking in LPE is that such an UHV environment that is ideal for *in situ* surface analytical for examining the substrate surface prior to epitaxial growth and providing a high degree of *in situ* growth control. In UHV condition, mean free path of electron beam is longer and can be used as a probe to monitor the substrate surface by means of non-contacting technique.

Although the corpuscular property of electrons is quite apparent, however, the wave-like nature of these particles is clearly shown in scattering by crystals. The details of their interaction with matter can be determined by the characteristic of the electron de Broglie wavelength and the atomic amplitudes. Consequently, the fundamental concepts of the theory of scattering and structure analysis of crystals are based on Fourier series and integral formalism [7].

Back diffraction high energy electrons can also be used to study materials, but the intensity of these electron decreases in proportion to the change in momentum on scattering. For a high energy electron beam incident normally on a surface the back diffracted beam is weak and the background intense so that the diffracted beams are hard to detect. However, if the high energy electron beam is incident on the surface at a grazing angle of less than 10° the momentum transfer is considerably reduced. This technique is known as reflection high energy electron diffraction (RHEED).

The advanced MBE systems mostly include RHEED in the growth chamber. The preparation of the growth surface of the substrate from the polishing stage to the in-situ cleaning stage in the UHV system is of crucial crystal perfection and with accurately controlled interfaces on an atomic scale.

RHEED technique has proven to be an important *in-situ* analytical tool for monitoring surface crystallography and studying MBE growth on the GaAs(100) and related surfaces. An incident high-energy electron beam created by electron gun, operated at 10-50 keV , with a small glancing angle. The electron beam then diffracted from the substrate surface and projected onto a fluorescent screen as shown in figure 2.5. The diffraction pattern

contains information from the topmost layers of the substrate or deposited material, and it can thus be related to the topography and structure of the growing surface.

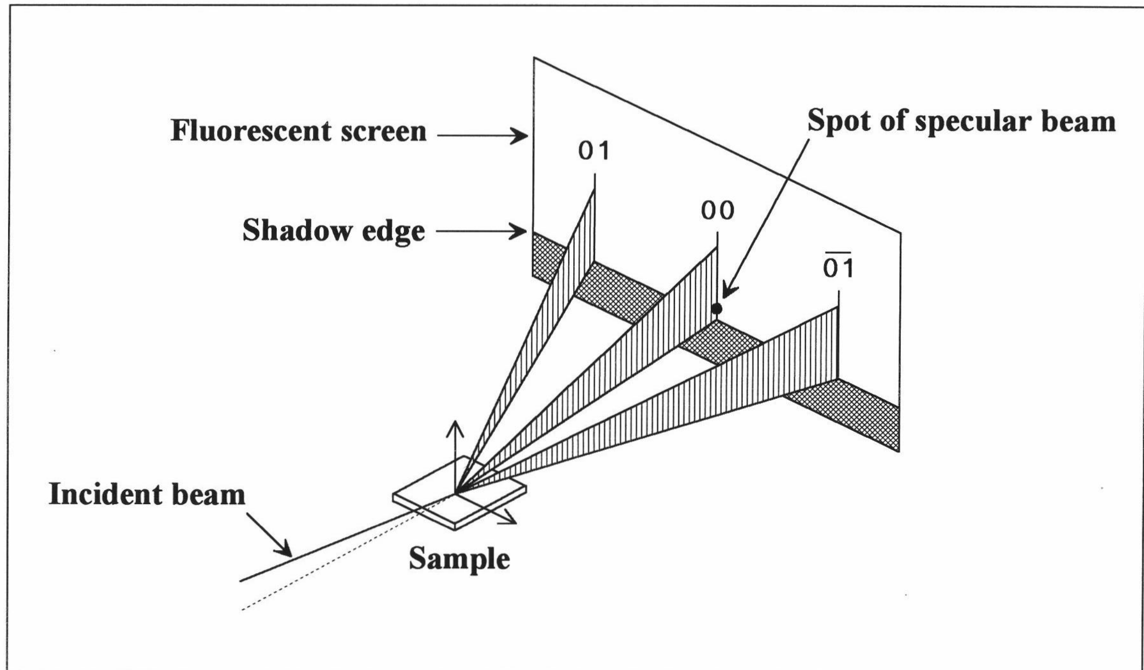

Figure 2.5 Geometric arrangement of RHEED *in situ* analytical tool.

The diffraction process in RHEED is in general not a true reflection. The scattered beam does not leave from the same surface where the incident beam entered. When most surface areas are rough then the diffraction pattern is produced in transmission through the surface asperities as shown in figure 2.6 (a) and represents many spotty features, while in the case of smooth surface the true reflection diffraction occurs as compared in figure 2.6 (b) shows the elongated streak patterns.

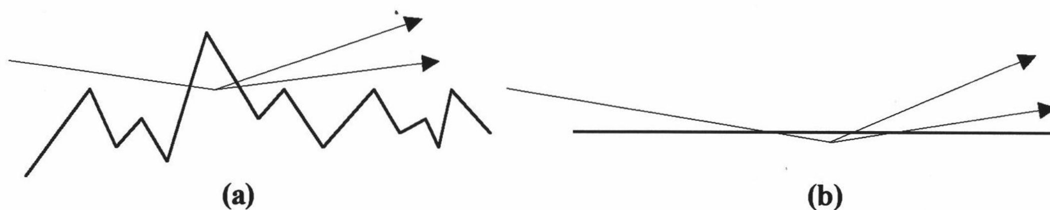

Figure 2.6 Transmission-reflection diffraction on rough surface (a) and True reflection diffraction on smooth surface (b).

Figure 2.7 is a photography of RHEED patterns from the fluorescent screen. This picture shows many of spots that are generated from the atomic scale rough surface of GaAs mirror-like substrate. The substrate is just heated up to around 500°C in the growth chamber. This temperature is not high enough to desorb oxide layers on the substrate surface that cause the roughness.

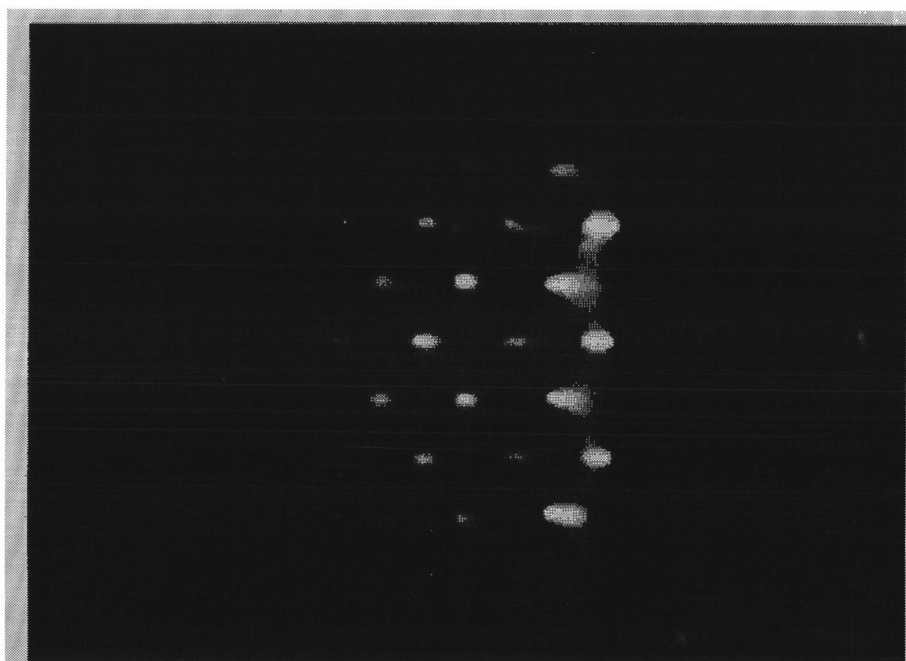

Figure 2.7 RHEED spotty-pattern of the oxide surface GaAs substrate.

The RHEED patterns change into the streak as shown in figure 2.8 after the substrate is heated until the oxide layers are fully desorbed this picture take at the substrate temperature 640°C. The GaAs substrate is mounted on an indium-free molibdinum block and the temperature is measured with thermocouple. These RHEED patterns using 20 kV electron gun in the growth chamber of RIBER 32P MBE installed at Max-Planck institute, Stuttgart, Germany.

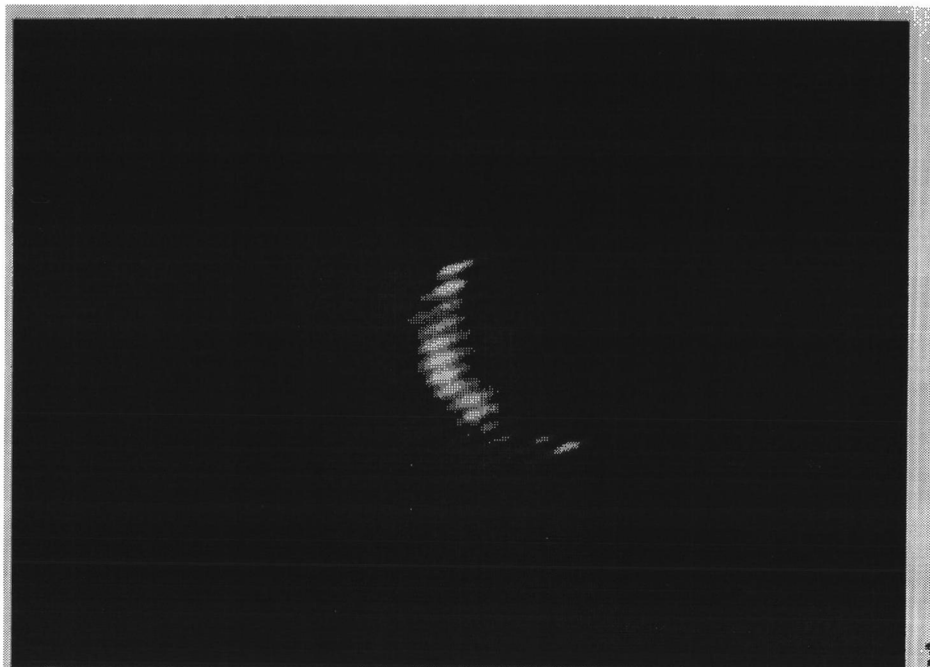

Figure 2.8 RHEED streaky (2x4) pattern of the GaAs clean surface.

The growing surface can be normally called in two forms, 2-dimensional (2D) and 3-dimensional (3D) surfaces. Appropriate growth process will produces 2D surface construction which obtained by surface equilibrium desorb-adsorb reaction. RHEED technique has a possibility to monitor the growing surface haven't any affectation. Whenever the spotty pattern received that means the 3D surface reconstruction occurs, growing process conditions should be adjusted until the streak pattern is recalled.

An ablility of RHEED specular beam is to examine an exactly period of layer-to-layer of the epitaxial growth. The oscillation of a specular spot intensity on the fluorescent screen is represents the formation of layers growing onto the surface. The period of the oscillation corresponds to the time required to deposit a lattice plane of GaAs (or $Al_xGa_{1-x}As$, AlAs, etc.) on the growing surface [8]. Just a lattice plane starts with statistically 2D islands having maximum specular beam intensity. The intensity of the beam decreases with increasing size of islands until to the minimum intensity at half-layer coverage. When the coverage is further increased islands coalesce more and more, and the intensity reaches a maximum again. This mode or RHEED is now widely used to calibrate and to monitor absolute growth rate in real time with monolayer resolution.