Molecular Beam Epitaxy of Gallium Antimonide

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Molecular beam epitaxy (MBE) is an extremely valuable thin film technique, which allows multilayer heterojunction structures to be grown with atomically abrupt interface and precisely controlled compositional and doping profiles. In this paper, we briefly describe the MBE technique and whole growth process of MBE with a gallium antimonide epitaxial layer.

1. Introduction

Molecular Beam Epitaxy (MBE) is a versatile technique for low dimensional semiconductor structures, optical and microwave devices preparing[1]. In MBE, thin films crystallizes via reactions between thermal atomic and molecular beam and a heated substrate under ultra-high vacuum (UHV) conditions. The film growth rate is typically 0.5−1.0 μm/h. It is chosen low enough that dissociation and migration of the impinging species on the growing surface to the appropriate lattice sites are ensured without incorporating crystalline defects. Due to the slow growth rate, change in composition and doping can thus be abrupt on an atomic scale alternative wording the eptaxial layers can be grown in atomic layer upon atomic layer. In this paper, we present MBE growth of GaSb, whose material is desirous to perform high quality infrared devices.

2. MBE Apparatus

The advanced MBE system mostly consist of three basic UHV building blocks, i.e. the growth chamber, the sample preparation chamber, and load-lock chamber, which are independently pumped and interconnected via large-diameter channels and isolation valves. Therefore the UHV can be maintained while changing substrate. The substrates can be moved between the chambers using magnetically coupled transfer rods. A liquid-nitrogen-cooled shroud is used to enclose the entire growth area in order to condense the residual water vapor and carbon-containing gases in the growth chamber during epitaxy. The substrate holder can rotate continuously to achieve extremely uniform epitaxial layer. Our MBE growth chamber for III-V compounds is shown in Fig.1, which is pumped to a pressure of approximately 10^{-9} Torr after extensive bake out (200℃, 72h). Rough pumping is achieved using rotary pumps. Then liquid nitrogen cooled, Ti sublimation pump, turbo molecular pump, ion pump and diffusion pump are used to perform final UHV pump.

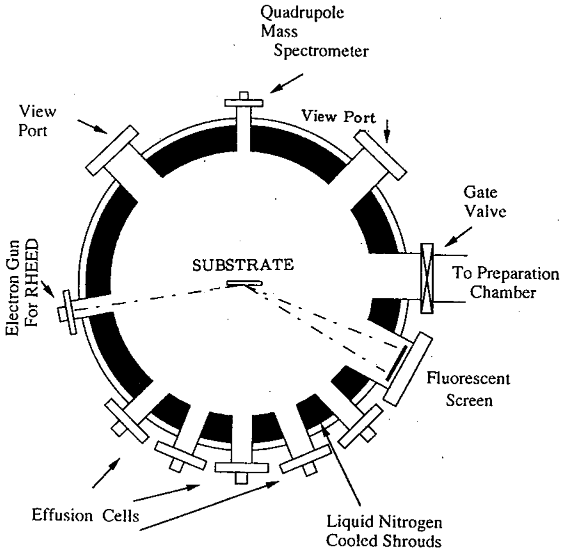

Fig. 1 Schematic cross-section of MBE growth chamber.

The growth systems are quipped with *in situ* surface analytical techniques. The most common facilities in the growth chamber are a quadupole mass spectrometer, which is convenient to have for detecting a leak in the vacuum system or to measure the water vapor background in the residual gas at all times, and a reflection high energy electron diffraction (RHEED) system, which gives important information about surface cleanliness, structure and proper growth conditions.

The experimental geometry of RHEED is illustrated in Fig.2. Electron having energy of typically 5−50 keV are incident on the substrate in a small glancing angle (1−3°) reflection mode. The diffraction pattern on the fluorescent screen mostly taken in [110] azimuth of (100) oriented substrate, contains information from the topmost layers of the deposited material and it can thus be related to the topography and structure of the growing surface. The diffraction would give streaks perpendicular to the shadow edge of the pattern, the spot diffraction implies that the surface texture is rough and the diffraction is from transmission through the protuberances. Additional features in RHEED pattern at fractional intervals between the bulk diffraction streaks manifest the existence of specific surface reconstruction, which are correlated to the surface stoichiometry and thus directly to MBE growth conditions. Figure 3 shows a diffraction in the [110] azimuth of the reconstructed GaSb (1×3) surface. The threefold periodicity is evident from the appearance of fractional-order (1/3, 2/3) streaks between the integral-order streaks, the surface structure depends on the incident fluxes of Ga and Sb as well as the substrate temperature[2]. The (1×3) surface is usually adopted for crystal growth.

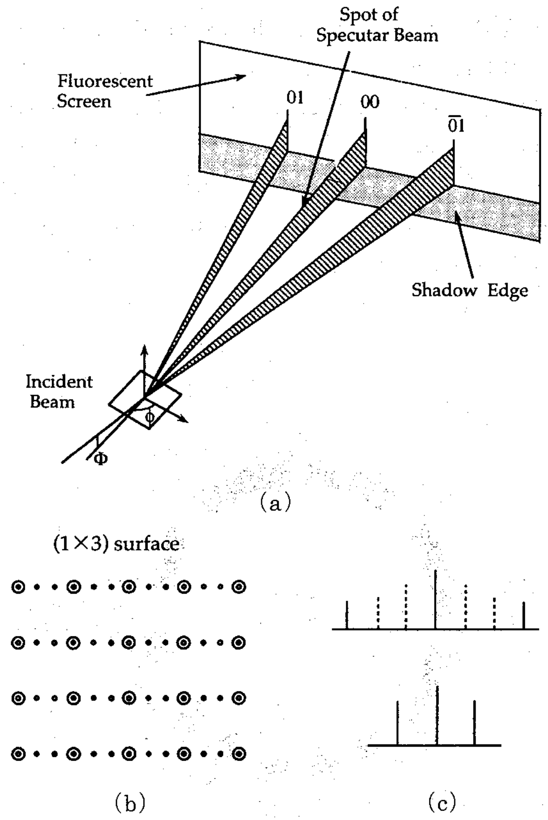

Fig. 2 Schematic diagram of RHEED geometry with grazing-angle incidence used as *in situ* analytical tool in MBE (a); surface unit cell (b); diffraction patterns of (1×3) reconstruction.

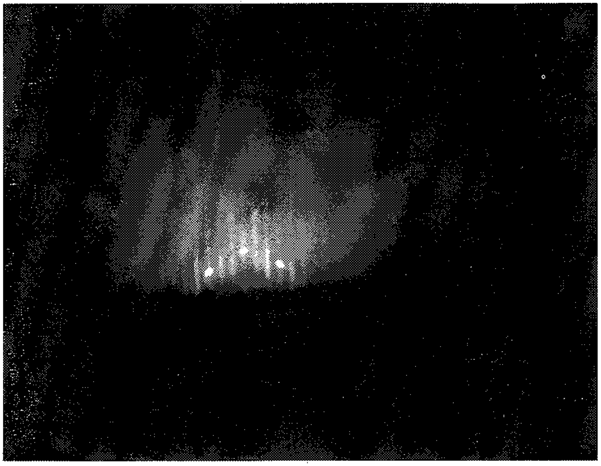

Fig. 3 Diffraction pattern from the GaSb(001)-(1×3) surface, in the [110] azimuth, taken at an electron energy of 20keV.

Another characteristic feature of RHEED pattern is the existence of periodic intensity oscillations during MBE growth[3]. The period of these oscillations corresponds exactly to the time required to deposit a lattice plane of epitaxial layer. It can be used to calibrate beam fluxes and control alloy composition and the thickness of quantum wells and superlattice layers.

3. The Process of GaSb Growth

GaSb (001) substrate is first organically cleaned with trichloroethylene, acetone and methanol sequentially. After rinsing in deionized water the substrate is then etched in solutions of $CH_3COOH : HNO_3 : HF = 20 : 9 : 1$ at room temperature for 40 sec., rinsed again in deionized water and then etched in $HCl : HNO_3 = 30 : 1$ (at 5℃ for 5 min.) to remove any oxide and organic materials on the substrate surface. Finally it is rinsed in deionized water for passivation[4] and blow dried with filtered nitrogen gas, the passivated oxide layer serves as a protection for the freshly chemically etched substrate from atmospheric contamination before epitaxial growth. The substrate is then mounted on a preheated (160℃) molybdenum sample holder with indium solder and load into the MBE system immediately. To grow high quality epitaxial layers, one must take meticulous care in substrate preparation, all above operation should perform in a clean ambiance and the MBE system has to be leak-free.

The epitaxial growth sequence of GaSb is shown in Fig.4. After a pump down of 10^{-7} Torr, the substrate were transferred to the preparation chamber and heated to 300℃ for 15 min. to be rid of moisture and air bubbles trapped in the In. Then the sample is entered to growth chamber, after the MBE system is pumped down, the liquid nitrogen shroud cooled and the effusion cells heated to the desired temperature (for Ga at 1000℃; for Sb at 380℃). In order for oxide desorption and surface reconstruction, the substrate is heated at 590℃ for 10 min. in antimony ambiance. At this point, the substrate is nearly atomically clean and ready for epitaxial growth. Next, the Ga beam is opened to begin the epitaxial growth.

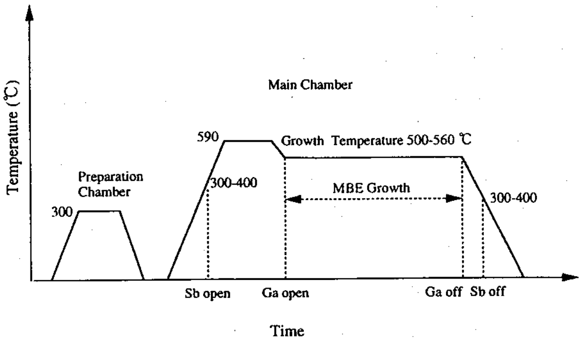

Fig. 4 Growth sequence of GaSb.

The basic process for MBE epitaxial growth of III-V semiconductor consists of a co-evaporation of the constituent elements of the epitaxial layer and of dopants onto the heated substrate where react chemically UHV conditions. The composition of the layer and its doping level depend mainly on the relative arrival rates of the constituent elements which in turn depend on the evaporation rates of the respective sources.

Joyce has[3] described the kinetic processes leading to the growth of GaAs from Ga and As_2 or As_4 molecules. The group III elements are always supplied as monomers by evaporation from the respective liquid element, and they have a unity sticking coefficient over most of the substrate temperature range used for film growth (500－630℃). The group V elements that are supplied as tetramers or dimers are more complex. It was found that, in general, group V molecular stick only when group III elements adatom plane are already established. The stoichiometric III-V semiconductors can be grown over a wide range of substrate temperature as long as excess group V molecular are impinging on the growing surface. The excess group V molecular do not stick on the substrate, and the growth rate of the film is only determined by the flux of the group III elements beam. The model is also valid for GaSb, and a number of other III-V compounds. According to the model, under excess Sb/Ga flux rations (3－5), we have grown single crystalline GaSb, while the Ga beam flux was controlled to give a growth rate of 0.76 μm/h. A good control of ternary III-III-V alloys can be achieved by supplying excess group V elements and adjusting the flux densities of the impinging group III beams. Fig.5 is the SEM image of AlSb/GaSb superlattices which we have grown using MBE.

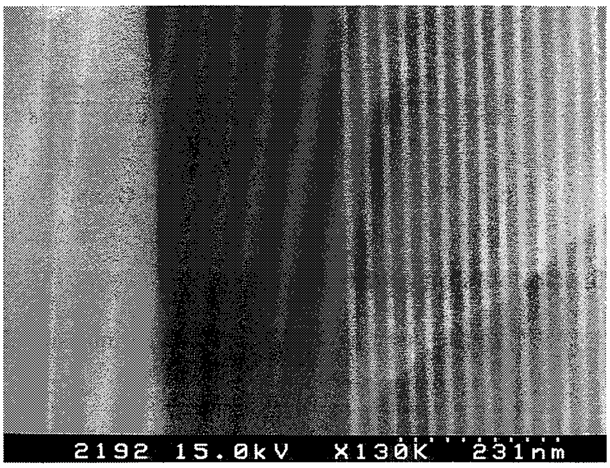

Fig. 5 SEM image of AlSb/GaSb superlattice grown by MBE.

4. Transport and Optical Properties

Unintentionally doped GaSb which is growth by MBE is p-type and is provided by native defects such as V_{Sb} or Ga_{Sb}-V_{Ga}[5]. The Hall effect was measured using van der Pauw method for the epitaxial GaSb layer grown on SI GaAs substrate. The hole mobility and density are 2700cm^2/V.s and 2.0×10^{16}cm^{-3} at 77K, and 630cm^2/V.s, 1.5×10^{17}cm^{-3} at 300K, respectively. The mobility is high as that reported by other workers[6].

Photoluminescence spectra of MBE GaSb was studied using an Ar-lasers (λ =514.5nm) with the sample held at cryogenic temperature (4.2K). The results are displayed in Fig.6. A sharp line at 795 meV is due to exciton bound to neutral acceptor (A^0-X). Three bands at 700 meV, 802 meV and 804 meV also originate from the recombination of electron-hole pairs bound to neutral acceptors, and a low intensity band at 808 meV comes from free-exciton luminescence. The sharp bound exciton peak implies that the MBE epitaxial layer have a good crystalline.

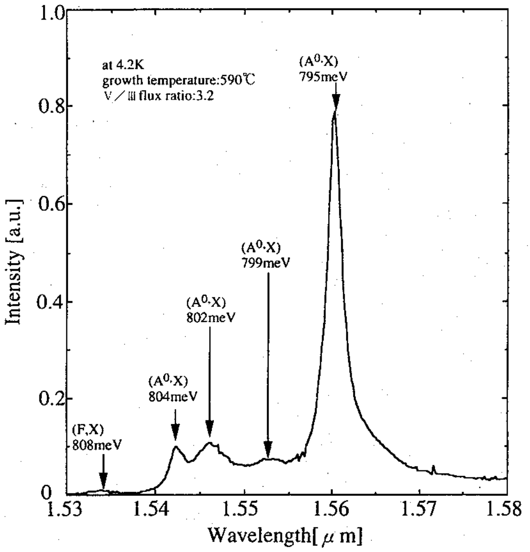

Fig. 6 Photoluminescence spectra of GaSb.

5. Conclusion and Future Work

MBE can be used to achieve extreme dimensional control in both chemical compositions and doping profiles, it is a powerful technique for new semiconductor structures and devices. In this paper, we have described the processes and techniques of MBE for GaSb growth, those results are also suitable to the other III-V semiconductors. The epitaxial layer show sharp exciton luminescence lines and the hole mobility is as high as 2700 cm^2/V.s at 77 K. The quality of the crystal is almost the highest that ever reported. There are still some problems that must be solved. For example, carrier concentration of undoped crystal is much higher than that is expected. This is due to high defect density and contamination with carbon, further studies on defects and impurities are necessary.

In future, we will pay our attention to GaSb related heterojunction and quantum well structures, such as (Al Ga)Sb/GaSb and In(As Sb)/GaAs superlattice, and GaSb/GaAs quantum dots that can grow in a self-organized way[7], which have potentiality for detector and lasers.

References

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