CHAPTER I

INTRODUCTION

1.1 Historical Background and Motivation

The invention of the transistor and the beginning of the computer age had an enormous impact on the science of materials. The new semiconducting devices were critically dependent on the availability of very perfect and extremely pure semiconductor crystals. The economic importance of the semiconductor revolution quickly stimulated researchers to develop a variety of new methods of growing crystals in order to produce the purity and perfection demanded by the new devices. One approach was to use a slice of semiconductor to deposit additional material in the form of a thin film in order to obtain electrical properties in the film that were superior to the starting substrate material. If the film had a crystalline structure that was ordered with the underlying substrate, it was described as epitaxial. Epitaxial films could be grown on a substrate of the same material, in which case the film was homoepitaxial. Alternatively, if grown on a substrate of a different material, the film was heteroepitaxial (Streetman and Banerjee, 2000).

Epitaxial films of semiconductors have continued to play a major role in device processing because they can be produced with electrical properties different from the substrate, either higher purity or fewer defects or with a different concentration of electrically active impurities as desired. By depositing a sequence of epitaxial layers with specific properties, specialized device structures can be realized without the need for processing steps involving the diffusion of impurities to produce doped layers. Many semiconductor materials can be grown epitaxially by allowing a suitable mixture of gaseous vapors containing the constituent elements to react with a heated seed or substrate crystal, a process known as vapor phase epitaxy (VPE). Placing a seed crystal wafer in contact with a liquid solution saturated with the semiconductor constituents can be used to grow an epitaxial layer by liquid phase epitaxy (LPE) as the solution is very slowly cooled. Each of these methods has its own advantages: VPE is a relatively rapid method of film growth which is readily scaled to manufacturing volume and LPE produces relatively pure films. However each has disadvantages as well, VPE takes place at relatively high temperatures which can enhance bulk diffusion and LPE does not produce films of uniform thickness (Bhattacharya, 1997). Besides these two processes, an experimental approach to epitaxial film growth was invented that is called molecular beam epitaxy (MBE). The localized beams of atoms or molecules of the constituents are provided to the depositing epitaxial film on a heated substrate under an ultra-high vacuum (UHV) environment. Generally, the MBE is equipped with the modern tools of surface analysis that can obtain real time information of the surface and its environment. As a result of these advantages, it has been a great experimental innovation more than other previous methods.

The growth of semiconductor thin films has a long history. Prior to the 1970s, these films were not structurally equivalent to bulk material but they were little used from a device standpoint. Since the 1980s considerable efforts have been devoted to realization of semiconductor heterostructures that provide carrier confinement in all three directions and behave as electronic quantum dots (QDs). The most straightforward technique is to use high resolution electron beam lithographic patterning of epitaxial layer structure for nanoscale patterning and dry or wet etching to make quantum wire (QWR) and QD structures by the end of the 2000s (Fujita et al. 1996; Jacobs et al. 1993). The QD structures fabricated through these techniques seem not to be satisfactory. It appears that etching-based technologies have a drawback that introduces damage and/or contamination by impurities into the crystals. Several modified techniques are to use the regrowth of epitaxial layers such as the fractional layer growth on the step edge of a vicinal substrate (Saito et al. 1993), selective growth on a pattern substrate (Sun et al. 2002), and cleaved-edge overgrowth (CEO) (Grundmann and Bimberg, 1997; Wegscheider et al., 1997). The QD structures fabricated by these techniques have advantages of no etching damage and no need fine lithography but still seem to have a drawback that is poor dot density for optical applications. Another growth process, known as self-assembled or self-organized growth is an alternative method of QD structure. One technique of this growth process was proposed by Stranski and Krastanow which is well known as SK growth mode. The SK growth mode has been used in heteroepitaxy to create islands on an initially two dimensional layer, including growth of islands relaxed by misfit dislocations in the strained epitaxy (Herman and Sitter, 1989). Another interesting alternative approach for the growth of self-assembled QDs, was proposed by Koguchi, is the droplet epitaxy growth. This technique involves with two processes for the III-V compound; the deposition process of group III elements droplets without the pressure of group V elements and the crystallization or incorporation process of group V elements into droplets to form the III-V nanostructures (Koguchi et al., 1993). This method can be used both in lattice-mismatched material system and in lattice-matched material system and can fabricate not only QDs but also quantum rings (QRs) and complex nanostructures with high crystalline properties such as GaAs (Mano et al, 2005), InGaAs (Lee et al., 2008), GaSb (Kobayashi, 2004), Ge (Cui et al., 2003), and InAs (Yoshida et al., 2004). Both of these self-assembled growth techniques are the center of interest in the semiconductor material and device research field now.

Quantum structures such as QDs and QRs are both interesting in quantum physics and device engineering. They are scaled-down structures of the electrical and optical devices and have possibility for developing the novel devices. The quantum properties of QDs make them a hopeful candidate for quantum information processing, for example coupled quantum dots (Mazur et al., 2005), quantum dot cellular automata (QCA) (Porod, 1997) and extended quantum dot cellular automata (EQCA) (Bajac, 2006). The ability to order and pattern QDs has been challenging. Several approaches, using artificial substrate process methods such as AFM local oxidation nanolithography (Martin-Sanchez, 2005), $AsBr_3$ *in-situ* etching (Songmuang et al., 2003) and scanning tunneling microscope (STM) probe-assisted nanolithography (Nakamura et al., 2000), have been developed to obtain templates for growing the groups of arranged QDs that are called quantum dot molecules (QDMs). These methods require complicated and expensive substrate processing equipments and are also prone to defects and contamination. In this thesis, we propose the fabrication of self-organized InP nanostructures in the form of ring-shaped QDMs in the matrices of $In_{0.5}Ga_{0.5}P$ grown on GaAs (001) substrates by droplet epitaxy technique using solid-source MBE. InP was chosen as a material for QD structure because its lattice mismatch with $In_{0.5}Ga_{0.5}P$ layer. In addition, droplet epitaxy technique can provide the circular-ring-shaped structure due to isotropic migrating atom property of In under P_2 pressure on $In_{0.5}Ga_{0.5}P$ layer during crystallization process. Therefore, the droplet epitaxy technique is favor for the growth of ring-shaped QDM structure. In droplet epitaxy growth, the initial dimension of the droplets, the atom migration and diffusion process determine the size and shape of the resultant nanostructures (Mano and Koguchi, 2005; Mano et. al., 2006). Hence, it is important to take a close look at the dimensions and the density of initial droplets and the crystallization condition. Therefore, the effects of growth conditions; indium thickness, indium deposition rate, deposition temperature and crystallization temperature, on physical and optical properties of self-organized InP nanostructures were investigated in this work. Atomic force microscopy (AFM) and photoluminescence (PL) measurements were performed to characterize the physical and optical properties of the InP nanostructures respectively. The densities of InP QDs, InP ring-shaped QDMs, outer and inner diameters of InP ring-shaped QDMs and the distributions of the number of InP QDs per InP ring-shaped QDMs, lateral size of InP QDs and height of InP QDs have been statistically reported. The PL intensity and FWHM reveals the density and uniformity of InP QDs at room temperature.

1.2 Objective

The objective of this work is study on the fabrication and the formation of self-assembled InP ring-shaped QDMs in the matrices of $In_{0.5}Ga_{0.5}P$ grown on GaAs (001) substrates by droplet epitaxy technique using solid-source MBE. This work focuses on the effect of the growth conditions with growth parameters of deposition temperature, crystallization temperature, indium deposition rate and indium thickness on the formation control and improve the uniformity of the InP ring-shaped QDMs.

1.3 Significant Benefits of the Research

1. The knowledge of droplet epitaxy technique that is cooperated with SK growth mode technique for InP ring-shaped QDMs formation by solid-source molecular-beam epitaxy.
2. The knowledge of capping layer growth technique using migration-enhance epitaxy technique accompany with conventional growth.
3. The information of surface morphologies and photoluminescence spectra of various conditions of InP ring-shaped QDMs growth.
4. The analysis and discussion of effects of growth condition (deposition temperature, crystallization temperature, indium deposition rate and thickness) on the properties of InP ring-shaped QDMs for improving new fundamental cell of EQCA.

1.4 Synopses

The thesis is organized as follows: The basic concepts of low-dimensional nanostructures are reviewed in chapter 2. This also includes theories of fabrication techniques and self-assembled QD formation, the principle of quantum information processing and GaAs, $In_{0.5}Ga_{0.5}P$ and InP characteristics. Chapter 3 gives the experimental details. The instruments that are used in this work are introduced. In chapter 4, results from experiments on the growth of $In_{0.5}Ga_{0.5}P$ layer and self-assembled InP ring-shaped QDMs are presented. The physical and optical properties of InP ring-shaped QDMs are based on atomic force microscopy (AFM) and photoluminescence (PL) results. The effects of growth conditions are discussed in this chapter. Finally, chapter 5 concludes this work.