A study of external patterning and internal forces in nanostructure growth

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**A STUDY OF EXTERNAL PATTERNING
AND INTERNAL FORCES
IN NANOSTRUCTURE GROWTH**

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Giving thanks to The LORD for His providence,

Liliana Tjahjana

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Abstract

Uniform and orderly arranged gallium arsenide (GaAs) islands on GaAs(100) substrate are demonstrated by the combination of external patterning in the form of nanosphere lithography and internal forces in the form of catalytic effects and facet formation. The substrate was patterned with an array of 210nm diameter silica nanodisks arranged in a hexagonal fashion with periodicity of 280nm. GaAs islands were found to grow from underneath the silica nanodisks, evolving from disk shape into eventually a pyramidal shape, resulting in the toppling of the supported silica nanodisks. The resulting GaAs islands were observed to follow the size and the arrangement of the silica nanodisks closely. The phenomenon occurred consistently for each nanodisk across a large area of $\sim 50 \times 50 \mu\text{m}^2$. The demonstrated island shape evolution also shows the potential for the growth mechanism to be used to obtain island shape tunability.

Taking the cue from the demonstrated catalytic growth, nanoscale patterning based on hydrogen silsesquioxane (HSQ) resist and Ti-Au nanometals have been realized. Upon exposure to electron beam, HSQ turns into non-stoichiometric silica (SiO_x), which is similar to the silica nanodisk mentioned before, thus a reasonable candidate to demonstrate island growth based on catalytic effect and facet formation. Gold is a well-known catalyst, thus is a good candidate to show catalytic growth not just for islands but also for odd patterns such as triangles, rectangles, and rings. HSQ nanopatterns as small as 20nm in lateral size and 42nm in height have been realized. Ti-Au nanopatterns as small as 23nm in lateral size and 20nm in height have been successfully lifted-off. These nanopatterns pave the way for growing quantum dots

and other nanostructure shapes through the demonstrated growth mechanism, thus moving a step closer to the nanotechnology dream where shape, size and arrangement of nanostructures are tunable down to nanoscale level.

Chapter 1: Introduction

1.1 Motivation

Semiconductor quantum dot has been a subject of interest since its discovery in the 1980s. Of the many desirable qualities that quantum dot offers, one major interest is on its delta function density of states, or atom-like density of states. This property renders it suitable for two major applications: first, as a gain medium in semiconductor laser because narrow density of states leads to narrow linewidth; or secondly as a single photon source in quantum computing, because its atom-like density of states makes it capable of emitting only one photon through recombination of a single exciton. We shall limit the scope of this work to III-V semiconductor quantum dots. The currently most successful fabrication method of III-V quantum dot is self-assembled growth mechanism in Stranski-Krastanov (SK) growth mode. This works quite well for applications in laser as the method is able to fulfill the major requirements of a laser gain medium, i.e. dense and uniform quantum dots, which gives enough gain and narrow linewidth. However the positions of the quantum dots on the surface cannot be controlled, i.e. the dots nucleate randomly on the substrate. This is one reason which renders SK method as less ideal in realizing single photon source, because one needs to be able to locate the dot to extract the single photon out of it. Therefore position control of quantum dot is essential for quantum dot single photon source. It would also be desirable to have position control for quantum dots in laser applications, to improve the repeatability of the quantum dot laser fabrication process.

1.2 Objectives

In this work, we will show a growth mode which utilizes the combination of external patterning and internal forces to realize uniform and position-controlled islands on a substrate. The term “islands” here refers to dots of larger size than quantum dots, of around 200nm in size. The islands do not yet display quantum effect but they serve as a “prototype” for quantum dots. The external patterning is realized by nanosphere lithography whereas the internal forces consist of: catalytic effect, facet formation mechanism, and lateral adatom adsorption. This growth mode has a potential to be used to realize both gain medium in laser as well as single photon source. The external patterning and catalytic effect are used for position control. Facet formation mechanism, lateral adatom adsorption and catalytic effect control the uniformity of the islands, which is potentially better than the conventional SK method. The catalytic effect therefore is responsible for both position control and uniformity.

Due to the interaction between these external patterning and internal forces, we will show that this growth mode is able to yield different shapes of islands. If the strengths of the internal forces can be controlled, the growth mode could then be utilized to achieve shape tunability of nanostructures. If the growth mode could also be realized at quantum dot scale, it would allow experimental studies of quantum effects as related to different quantum dot shapes. Most of these studies are currently limited to theoretical form, thus experimental verification is desirable in this field of research. We will also explore the idea of realizing shape tunability on a single sample, which would increase the information content. To realize this, we will attempt to pattern different shapes using electron beam lithography.

1.3 Major Contributions

The possibility of combining external patterning and internal forces to achieve uniform and position-controlled islands have been proposed and studied. Uniform and orderly arranged GaAs islands within an area spanning tens of microns have been achieved. A model to describe the growth phenomenon has been proposed. Alternative patterned substrates to realize the growth phenomenon with sub-50nm pattern size have also been fabricated and their potential applications discussed.

From this work, 1 journal paper and 1 conference proceeding have been published. This work was also presented on two international conferences.

1.4 Organization of Thesis

Chapter 1 presents the background and motivation of this work. Chapter 2 gives a background information of the research related to this thesis. Chapter 3 contains descriptions on the experimental techniques used in this work. The process lines to fabricate the patterned substrates are discussed in Chapter 4. The results of the growth on the patterned substrates are elaborated in Chapter 5. Finally, conclusion and recommendations for future work are presented in Chapter 6.

Chapter 2: Background Information

It is well known that optoelectronic properties of a semiconductor start to change significantly from its bulk counterparts when they are scaled down in size. Starting from the invention of quantum well which provides one-dimensional confinement for electrons, many attempts have been proposed and demonstrated to increase the degree of electronic confinements, such as in quantum wires [1-3], quantum dash [4-6], and even quantum dots [7-9], for various purposes ranging from solar cell [10-12], low threshold semiconductor laser [13-15], efficient optoelectronic modulator or switch [16-18], high efficiency displays [19-27], bioimaging application [28-30], to a more fundamental research such as manipulating quantum information for quantum computing applications [31-32].

The effect of scaling down gives rise to the emergence of quantum phenomenon where the semiconductor carriers (i.e., electrons and holes) are trapped inside a potential well formed by a sandwich of two materials of different energy bandgaps, resulting in quantization of carrier energy levels. For the purpose of illustration, the potential well is schematically drawn in Fig. 2.1(a), and the requirement for an electron to exist in the well is to satisfy the resonance condition in the well, i.e., $kL=n\pi$. Here, L is the size of the potential well, k is the electron wavenumber, and n is the integer number. The energy level E_n associated with the above resonance condition can be written as [33]:

$$E_n = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m} = \frac{h^2}{8m} \left(\frac{n}{L} \right)^2 \quad (2.1)$$

where h is the Planck's constant and m is the electron mass. The simplistic representation of a quantum well is shown in Fig. 2.1(b), which can be seen as potential wells in both conduction and valence bands. The discrete energy levels imply restricted energy transition from valence band to conduction band and a dramatic change of the carrier density of states, which is of great importance to light-matter interaction.

Figure 2.1. (Adapted from Ref. 33) (a) Schematic of a potential well and its corresponding electron wavefunction, (b) simplistic representation of a quantum well.

Fig. 2.2 shows different quantum structures and their resulting change in the density of states in comparison with the bulk semiconductor [Fig. 2.2(a)]. In the quantum well structure [Fig. 2.2(b)], the carriers are confined in one direction, while freely wandering along the other two directions. The density of states (DOS) change into a staircase-like distribution which follows the envelope originated from bulk properties. If the carriers are confined further in one more dimension, such as in quantum wire structure [Fig. 2.2(c)], one can see that the DOS reduces to asymmetrically sharp peaks. Finally, if the carriers are confined in the one last

direction, i.e., in quantum dot structure [Fig. 2.2(d)], the DOS can be seen to reduce into delta-like function.

Figure 2.2. (Adapted from Ref. 34) Comparison of dimensionality, confinement extent and density of states of: (a) bulk, (b) quantum well, (c) quantum wire, (d) quantum dot.

This dramatically increases the strength of light-matter interaction which has been shown to reduce the lasing threshold current, decrease laser linewidth, and increase of sensitivity in photodetector. This can be seen from the energy point of view where the carrier movement implies continuity in the energy spectrum. This means that there is an absence of carrier movement in discrete energy levels, at least in ideal condition (in realistic condition, however, each energy level is intrinsically broadened due to crystal vibration and Heisenberg uncertainty principle). Thus, light-matter interaction is more probable in quantum mechanical sense when the carriers are localized compared to the case when the carriers freely move in all directions. Furthermore, the confined movement of carriers decreases the effect of temperature (which imparts more crystal vibrations) in device performance.

Figure 2.3. (Adapted from Ref. 35) Density of states, gain spectrum and cavity loss in (a) bulk; (b) quantum well; (c) quantum wire and (d) quantum dot laser.

In addition to strengthening light-matter interaction, quantum structures provide more tunability in lasing wavelength. Fig. 2.3 shows the effect of modified DOS to the lasing wavelength in different quantum structures. In the bulk, lasing only occurs

when oscillation condition is satisfied, i.e., cavity loss is equal to the gain, which happens only at particular wavelength (or energy). The increase in gain (or current) shifts the gain peak to higher energy, which means the laser emission wavelength is dependent on current. This is not the case in quantum structure, where the energy at which oscillation condition occurs is determined by the sharp peaks of the density of states which makes the gain peaks relatively independent from gain (or current). It can also be seen that an increase of confinement gives more precision in the light emission wavelength. The quantum dot energy levels can be deduced by generalizing Eq. (2.1) in three dimensions [33],

$$E = \frac{h^2}{8m} \left[\left(\frac{n_x}{L_x} \right)^2 + \left(\frac{n_y}{L_y} \right)^2 + \left(\frac{n_z}{L_z} \right)^2 \right], \quad (2.2)$$

where n_x , n_y , and n_z are the quantum numbers and L_x , L_y , and L_z are the sizes of the quantum dot. Therefore, apart from tuning the material composition of the quantum dot, the light emission wavelength can also be readily tuned by changing the size of quantum dots. Indeed, this serves as another advantage of using quantum structure in applications utilizing light-matter interaction.

Quantum dots can be realized in both II-VI and III-V compounds. In the II-VI compounds, the quantum dots are typically synthesized inside a certain liquid solutions, commonly termed as colloidal quantum dots. Examples of II-VI quantum dots are CdS, CdSe, CdTe, PbSe, ZnO, ZnS, ZnSe, and ZnTe. Because the bandgap of most II-VI quantum dots is within the visible wavelength, the applications of II-VI quantum dots are mostly in solar cells, bio-tagging in image processing, and display technology. The advantage of using II-VI compounds is the relatively lower processing cost since it does not involve crystal growth, however, the limitation can

be found in their visible light emission wavelength which is not applicable for optical communication which requires infrared wavelength range. Recently, however, II-VI compound has gained significant interest in developing single photon source where a single quantum dot directly correspond to a single optical nanocavity, rendering the interaction of only one exciton (which resembles an atom) and one photon [36]. The example of II-VI compound of near infrared light emission wavelength is lead sulphide (PbS).

The III-V semiconductor quantum dots, on the other hand, are normally fabricated by self-assembled growth mechanism in Stranski-Krastanov (SK) growth mode. The examples of III-V semiconductor compounds are InAs, InGaAs, GaP, GaN, GaAsN, AlGaAs, AlGaN, and GaInNAs. Apart from applications related to laser, photodetector, and modulator, quantum dot is also an attractive choice to be used as single photon source for quantum cryptography in optical communication purposes [37]. This is particularly interesting since III-V semiconductor provides light emission wavelength within infrared range.

SK mode is a mode of epitaxial growth in lattice-mismatched systems. There are three modes of epitaxial growth, depending on the relative strength of interface energy (γ_i), surface energy (γ_s), and film energy (γ_f) [38]:

1. Frank-Van der-Merwe or layer-by-layer or two-dimensional growth

This growth takes place when substrate surface energy is stronger than the sum of epitaxial layer surface energy and interface energy ($\gamma_s > \gamma_i + \gamma_f$). Therefore, the deposited atoms tend to stick to the substrate surface than to the epitaxial layer

surface, resulting in 2-dimensional growth. The pseudomorphic growth will continue until reaching a certain critical thickness whereby formation of dislocation is energetically more favoured.

2. Volmer-Weber or three-dimensional growth

In contrast to two-dimensional growth, Volmer-Weber growth takes place when substrate surface energy is lower than the sum of epitaxial layer surface energy and interface energy ($\gamma_s < \gamma_i + \gamma_f$). Rather than sticking to substrate surface, the deposited atoms prefer sticking to themselves to form three-dimensional islands.

3. Stranski-Krastanov (SK)

When the system has small interfacial energy but large lattice mismatch, the total energy of the system is lowered by forming isolated islands. The first few monolayers occur in layer-by-layer mode. Upon reaching a certain thickness, three-dimensional growth is more favoured.

Figure 2.4. (Adapted from Ref. 34) Three modes of epitaxial growth: (a) Frank-van der Merwe; (b) Volmer-Weber; (c) Stranski-Krastanov.

The comparison of the above three growth modes is shown in Fig. 2.4. SK growth of QD is driven by strain, which results from lattice mismatch between QD active

material and underlying material, could be the barrier material or another material which is deliberately set as stressor layer. First an epitaxial layer whose lattice constant is larger than that of substrate is grown pseudomorphically on the substrate. This layer is called wetting layer. As the thickness increases, after a few monolayers, and at a certain process window, the strain gets larger and finally at a certain critical thickness, two-dimensional growth is no longer favourable energetically. As a relaxation method, three-dimensional growth of a hump of quantum dot takes place. The quantum dot will consume part of the wetting layer. Subsequently, on top of the quantum dot layer, a layer of larger bandgap material is grown to form top barrier layer. This step is called capping. The quantum dots maintain the epitaxial structure until a certain point where the strain relaxes, creating undesired dislocations.

Figure 2.5. (Adapted from Ref. 39) QD laser developed by QDLaser, Inc.

The nucleation of QD in SK growth mode is purely due to internal force in the form of strain within the material, not due to any external force. The nature of this nucleation strongly depends on the growth conditions consisting of thermodynamic

and kinetic effects. These self-assembled quantum dots are dense and uniform to a certain extent, which gives enough gain and narrow linewidth for laser. Quantum dot laser has been commercialized by QD Laser, Inc. using self-assembled quantum dots as the gain medium [39]. The QD laser structure is as seen in Fig. 2.5. However one drawback in SK growth mode is that the quantum dots nucleate randomly on the substrate such that one has no control over the positioning of the quantum dots. For this reason, SK method may not be a suitable choice to realize single photon source, because one needs to be able to locate a dot before being able to extract a single photon out of it.

Figure 2.6. From Santori et al. [40], pillar microcavity structure containing self-assembled quantum dot as the gain medium: (a) schematic; (b) SEM of actual pillar structure.

There are two ways to get around this problem, first, by randomly create devices on the sample grown with self-assembled quantum dots where by chance, there will be a few devices where each contains one or a few quantum dots in it, e.g. work done by Santori et al. [40]. In this work (see Fig. 2.6), self-assembled quantum dots are grown on series of GaAs/AlAs Distributed Bragg Reflectors (DBR) and then capped by

another series of GaAs/AlAs, to create a microcavity device. Afterwards, sapphire dust particles are sprayed on the surface as etch mask. The resulting structure after etching is randomly arranged photon emitters, where each pillar statistically contains one or a few quantum dots. It is to be expected that this method has low yield, and there is no way to accurately locate and address one particular pillar.

The second way to get around the problem of applying self-assembled quantum dots for single photon emitters, is to use a patterned substrate, e.g. creating artificial nucleation centres on the substrate where each centre is addressable, before growing the quantum dots. One such successful implementation is done by S. Kiravittaya, et. al. [41] where a pattern of holes is etched into the GaAs substrate using Electron Beam Lithography (EBL) and Reactive Ion Etching (RIE). The quantum dots nucleate preferentially at the holes and afterwards capped. For the purpose of imaging, another layer of quantum dots is grown on top the first QD layer, where each quantum dot nucleate preferentially on top of the underlying quantum dot. The resulting quantum dots are as seen in Fig. 2.7.

Figure 2.7. From S. Kiravittaya et. al. [41]: (a) AFM image of ordered InAs QD array on GaAs (001) substrate. The inset shows a magnified image; (b) Height and diameter histograms of the ordered QD array shown in (a).

Patterning the substrate also helps to improve the linewidth of the QD light emission when more QD layers are grown, as shown by another work by Kiravittaya et al. in Ref. 42 where the PL linewidth improves from 32.8 meV to 22.7 meV for 11 stacks of QD layers.

As shown in Fig. 2.7, the positions of the quantum dots are well controlled. However, EBL is a serial writer, hence this method is time-consuming for applications requiring large density of quantum dot emitters. On the other hand, self-assembly is a parallel process, where many nanostructures are created simultaneously at a time. Therefore, trade-off between density and addressability will always be present in patterning methodology.

This trade-off is alleviated by the use of nanosphere lithography, which uses nanospheres arrayed in a close-packed fashion on the substrate, by spin-coating or other methods, to serve as etching mask [43-45] or deposition mask [46-47]. By carefully tuning the process conditions, a large area of close packed and orderly arranged nanospheres can be obtained. The example of hexagonally close packed polystyrene nanospheres is shown in Fig. 2.8. Nanosphere lithography can then serve as a template for quantum dot growth. It is also possible to reduce the size of the nanospheres, for example polystyrene nanosphere size can be reduced using O₂ plasma treatment, thus adding another parameter control to the process.

Even though etching through the nanosphere pattern to form the quantum dots seems to be a logical step, it has been well known that top-down lithography method to form quantum dots is not ideal due to defects introduced at the sidewall of the

quantum dot, thus creating non-radiative recombination centres. Another way is to use the nanosphere pattern to etch into the substrate to form holes as a template for growing the quantum dots, similar to Ref. 41 before. However, growing quantum dots from patterned holes is also not an easy task because of the atomic steps introduced on the sidewall of holes, rendering the quantum dots nucleated on the holes to be non-uniform [48-50]. This is where catalytic effect and facet formation can play a role. It is to be noted that the catalyst is externally introduced, but the response of the system to the catalyst can be considered as an internal force.

Figure 2.8. From Ref. 47, large area of close-packed monolayer PS nanospheres.

Catalytic growth of III-V semiconductor compounds have been mostly dedicated to growth of nanowires [51-53]. In this project, we will attempt to use the catalytic effect and facet formation to grow islands instead. Nanosphere lithography is used as the external patterning to define the positions of the islands, whereas the catalytic effect and facet formation serve as the internal forces to grow the islands. We will

also show the possibility of nanostructure shape tunability through the use of catalytic effect and facet formation. Tuning the size, shape and arrangement of nanostructures is one of the visions of nanotechnology. Of special interest is quantum ring [54]. With quantum ring one can mimic the resonance properties of a smaller quantum dot without having to go down to the scale of quantum dot.

As a step further, to demonstrate the tunable shapes and sizes in a single sample, we will use the electron beam lithography. In this case, using electron beam lithography as the external patterning is more efficient than using nanosphere lithography because for nanosphere lithography, uniformity in arrangement and the number of size variations are closely linked. In other words, using nanosphere lithography it is difficult to achieve size variation within a single sample while maintaining the uniformity in arrangement. For electron beam lithography, uniformly arranged and sized patterns can be defined regardless of the number of size variations of the patterns in a single sample.

Summary

In this chapter we have briefly reviewed basic theoretical understanding of quantum dot, the quantum dot material system, and the applications of the quantum dot properties into light emitting applications mainly laser and single photon source. We have also reviewed various quantum dot fabrication methods, mainly the self-assembled quantum dots and discussed their limitations. Considering these limitations, we propose an alternative growth method which is to combine the external patterning in the form of nanosphere lithography; and internal forces such as catalytic effect and facet formation. Before moving on into the details of the growth,

in the next chapter brief descriptions on the fabrication and characterization techniques used in this work will be given.

Chapter 3: Experimental Techniques

This chapter describes some of the fabrication and characterization techniques used in this work, with emphasis on the techniques particularly used to cater to our purposes.

3.1 Solid Source Molecular Beam Epitaxy (SSMBE)

Molecular Beam Epitaxy (MBE) is a technique to grow precise thickness of epitaxial layer where an elemental source is evaporated and since the system is kept at ultra-high vacuum, the source molecules or atoms travels like a beam to the growing surface and form the epitaxial layer on the surface. When the growth material is solid elemental sources, the MBE is categorized as Solid-Source MBE. The MBE system which we used in this project is RIBER-32, which is an SSMBE. The schematic drawing of our SSMBE is shown in Fig. 3.1, which shows the important components of SSMBE.

MBE relies on Reflection High-Energy Electron Diffraction (RHEED) as an in-situ monitoring system to determine the start of the epitaxial growth, which is when the native oxide layer of the sample to be grown is completely desorbed by heating in the growth chamber. When the RHEED shows 2x4 reconstruction, physically a streaky diffraction pattern as seen from the phosphorus screen, which is a characteristic of a flat epitaxial layer, growth can then be started.

Figure 3.1. Schematic of Molecular Beam Epitaxy (MBE) system used in this project, showing its important components.

Because our starting substrate is a patterned substrate, the RHEED pattern will not be a 2×4 reconstruction. Instead, we have bonded a dummy flat substrate, side-by-side to the patterned substrate. Now, the electron source is directed to this dummy substrate instead. If both the substrates are pre-treated in the same condition, we can safely assume that when native oxide on the dummy substrate has been completely removed, the native oxide on the GaAs surface of the patterned substrate has been completely removed as well.

3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is an indispensable measurement tool in dealing with nano patterns on a surface. In fact, in quantizing lateral sizes of grown islands, the SEM inspection should precede all other analysis since SEM gives the physical image of the sample. The principle of imaging in SEM is based on secondary electron emissions generated from electron beam irradiation. These

secondary electrons are generated from shallow depths of the sample, which makes them sensitive to topography. The secondary electrons are then collected by the secondary electron detector by means of a positive bias. When the intensity of the signal obtained from the secondary electrons is synchronized with the movement of the raster beam, a topographic image is obtained.

3.3 Electron Beam Lithography (EBL)

Electron Beam Lithography is an extension of scanning electron microscopy whereby electron beam radiation is used to make patterns instead of imaging. The electron beam is focused onto the material sensitive to electron beam radiation, commonly termed as electron beam resist. The effect of radiation can be seen from the fact that the electron collides with the resist molecules, forming forward and backward scatterings. The forward scattering occurs more frequently than the backward scattering, and it contributes more to electron beam dose which is defined as the amount of charge stored after certain beam exposure time (i.e., $\mu\text{C}/\text{cm}^2$). Theoretically, the resolution of electron beam can be as small as one electron wavelength ($\sim 0.1\text{nm}$), however practically the resolution is limited by the molecular size of the resist material, which is in the order of $\sim 10\text{nm}$. Similar to its optical counterparts, the electron beam resist can be of positive or negative tone. The positive and negative resists that were used in this thesis is briefly described in this section.

In positive tone resist, the high energy electron beam breaks the bond of the resist material (also known as the chain scission), rendering the resist material to dissolve faster in developer solution in contrast to the un-exposed areas. Notable examples of

positive tone resists are PMMA 950K (MicroChem), and ZEP520A-7 (Zeon). In negative tone resist, the electron beam crosslinks the bonds of the resist materials, instead of breaking it. Naturally, the energy required for breaking the molecular bond is lower compared to that for crosslinking the molecular bond, which translates to the fact that higher electron beam dose is always required for negative tone resist. Inside the developer solution, the un-exposed areas will be dissolved, leaving the crosslinked parts (the exposed areas) on the sample. Notable example of negative tone electron beam resist is hydrogen silsesquioxane (HSQ).

As will be shown in this thesis, both positive and negative tone resist are useful for different pattern definition. The positive resist is used to for metal nano-patterning, which is to be used as the template for island growth. The negative resist, on the other hand, is used for patterning sub-100nm SiO₂ nanodisk. These two methods will be discussed in Chapter 4. The Electron Beam Lithography system used in this project is the Raith e-LiNE (from Raith GmbH) situated at Cleanroom 2 in Nanyang Nanofabrication Center (N2FC) in the university.

3.4 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is the imaging method which uses cantilever to characterize the surface morphology of a sample. The term “atomic force” originates from the fact that the Van der Waals force between the cantilever and the surface is used to conformally map the surface of the sample. The cantilever scans across the sample in two modes: contact mode and non-contact mode. In contact mode, the cantilever is controlled by a feedback mechanism to maintain constant atomic force with the sample surface, which translates to a constant deflection of the cantilever.

As a result, as it is driven to scan across the sample, the height of the cantilever changes with accordance to the sample topography. A laser beam is shined to the cantilever top and the reflection is recorded by a photodetector. Synchronizing this with the sample stage movement, a topographic image and height data are then obtained.

In non-contact mode, the cantilever is oscillated at or close to its resonance frequency. As it is brought close to the sample surface, the atomic force from the sample surface changes its oscillation amplitude, phase and resonance frequency, and the change is sent to the feedback system. To maintain constant oscillation characteristics, the tip-to-sample distance is adjusted by the feedback system. Therefore when the cantilever oscillation characteristics are maintained across the sample, a topographic image and height data are obtained.

Although it is possible to obtain three dimensional data in AFM, it should be noted that the measured lateral dimensions are convoluted with the finite size of the cantilever tip. The convolution effect can be compensated in the AFM software, however, this method is shown to be ineffective when dealing with nano-sized patterns. In this project, the AFM system used is Digital Instruments Nanoscope where non-contact mode is used. Although AFM gives a topographic image, it is inaccurate to use AFM to collect lateral size data of islands due to convolution between the AFM tip and the sample surface. Therefore in this project AFM is solely used to obtain height data of the islands.

3.5 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is used to determine the composition of the grown islands. The basic principle of XRD is Bragg diffraction. When X-ray is radiated on atoms, the atoms will reradiate waves of same frequency. The re-radiated waves will interfere constructively or destructively, producing diffraction pattern. As the diffraction intensity is plotted against the incident angle of the incoming X-ray, each peak position corresponds to the spacing between a particular atomic plane (or crystal plane) of the crystal. Comparing this to a known standard of crystal plane spacings, the composition of the crystal can be inferred.

3.6 Dry Etcher: Reactive Ion Etching (RIE) and Inductively Coupled Plasma Reactive Ion Etching (ICP-RIE)

Dry etching technique is used in our project to pattern SiO_2 nanodisk with polystyrene nanospheres as the hard mask. The main principle of Reactive Ion Etching (RIE) is to use gases which are made into plasma state when subjected to RF oscillation (13.56MHz). The etching rate depends on the RF power, gas composition, and plasma density. The RF power determines the etching directionality (or anisotropy), which means higher directionality can be obtained by higher RF power.

In the RIE system, the plasma density and etching directionality are both determined by the RF power. This renders the limitation of RIE system, since increasing the plasma density leads to the increasing roughness on the surface. This is not the case when additional RF circuit is incorporated into the system, which is often called ICP-RIE. In this system, the directionality is solely determined by the RF power, while

the plasma density is determined by the ICP power. With this independent control, the etch rate can be dramatically increased without having trade-off with surface roughness.

It should be noted that etching only takes place when the byproduct of the chemical reaction with the etchant is volatile at a given temperature and pressure. As the volatility depends on the vapor pressure of the chemical, it is instructive to keep the etching at low pressure. In some cases, however, low pressure is not enough and substrate heating is required to ensure the volatility of the etching byproduct. In this project, the dry etching is done by AST Clen-100 and Oxford Plasma80Plus.

3.7 Electron Beam Evaporator

Electron Beam Evaporator is used to deposit gold catalyst. The principle of electron beam evaporation is the use of focused electron beam to heat up metal source in a crucible placed in a vacuum chamber. As a result, the heated metal evaporates and re-deposits on the sample placed above the metal crucible. For reliable lift-off, it is important to have reasonably long distance between metal source and the sample. This is because the directionality of the evaporated metal is improved as it goes further up. Furthermore, longer distance means the temperature around the sample is cooler which prevents the mask crosslinking. The second important aspect is in preconditioning the pattern before depositing the metal, which requires a degree of undercut (this will be explained in Chapter 4). The electron beam evaporator used in this project is Edwards HHV Auto 306 Turbo.

3.8 Fourier Transform Infrared Spectroscopy (FTIR)

Energy transition between some molecular vibrational states corresponds to infrared portion of electromagnetic spectrum. The transition is characteristic to the given bond. Therefore by shining infrared light on a sample and collecting the resulting absorption spectrum, one can identify the bonds in the sample and determine the types of materials present. For example, stoichiometric SiO₂ show three peaks on its infrared absorption spectrum corresponding to different vibrational states of Si-O-Si bonding: stretching vibration at 1080cm⁻¹, bending vibration at 800cm⁻¹, and rocking vibration at 450cm⁻¹. To shorten the measurement time, all infrared frequencies are shined on the sample simultaneously and Fourier Transform calculation is used to produce absorption intensity vs. frequency plot. The FTIR system used in this project was IRPrestige-21 from Shimadzu.

3.9 Plasma-Enhanced Chemical Vapor Deposition (PECVD)

Plasma-Enhanced Chemical Vapor Deposition (PECVD) is a thin film deposition technique where the precursor gases' decomposition and reaction rate is enhanced by being ignited into plasma state. The ignition is usually done by RF techniques. The precursor gases react and form a thin film on a substrate. The PECVD systems used in this project were Unaxis Nextral D200 (in IMRE) and PlasmaTherm790 (in NTU).

3.10 Summary

In this chapter we have reviewed some of the important fabrication techniques used in this work, namely: MBE, EBL, PECVD, RIE, ICP-RIE, and e-beam evaporator. The important characterization techniques used in this work are namely: SEM, AFM,

XRD, and FTIR. In the next chapter, we will report our substrate patterning work which was done using these fabrication and characterization techniques.

Chapter 4: Fabrication of Patterned Substrates for Catalytic Island Growth Demonstration

In this chapter, various patterning techniques were explored for the purpose of demonstration catalytic growth. There are two kinds of patterning methodology, (1) the parallel processing types, and (2) the serial processing types. In the first method, the pattern is typically made out of self-assembly or colloidal method which gives rise to a hexagonally closed pack patterns with a certain degree of uniformity in their sizes and arrangements. Here, the patterns are simultaneously obtained, making it a high throughput method. However, this comes at the expense of the lack of information contained in the pattern. In the second method, each of the patterns is written in a sequential manner. Here, each of the patterns can be uniquely defined in terms of size, shape, and arrangement, thereby adding degrees of information in the pattern.

Thus, one immediately finds that there is inherent trade off in both methods. Patterns with single information consisting of uniform sizes and shapes situated in periodic geometrical arrangements are obtained in short processing time, while patterns with multiple information consisting of variable sizes, shapes, and geometrical arrangements are obtained in a long processing time. Thus, both methods have their strengths and weaknesses and none is more superior to the other.

4.1 Nanosphere Lithography-based Patterned Substrate

4.1.1 Spin-coated Polystyrene Nanospheres

An SiO₂ nanodisk array was fabricated by means of nanosphere lithography [1] which was developed in collaboration with Institute of Materials Research and Engineering, Singapore. The process line to fabricate the patterned substrate is shown schematically in Fig. 4.1.

Figure 4.1. Schematic illustration of nanosphere lithography (adapted from Ref. 1):

(a) spin-coating PS nanospheres on PECVD SiO₂-coated GaAs substrate; (b) reducing the size of the nanospheres by RIE; (c) RIE etching of the SiO₂; (d) etching away of the PS nanospheres, leaving the disk-shaped SiO₂ on the GaAs substrate.

First, a 60-nm-thick layer of SiO₂ was deposited on GaAs (100) substrate by plasma enhanced chemical vapor deposition technique (PECVD). The system used was Nextral D200 PECVD from Unaxis. The gases used were 30 sccm of SiH₄, 400 sccm of N₂O, and 184 sccm of He. The pressure was 730mTorr and RF power was 100W. The substrate temperature was set to 280°C and the deposition rate was 200 nm/minute.

A water-based solution containing 300nm diameter polystyrene (PS) nanospheres was then spin-coated on the SiO₂. This resulted in a large area of the sample surface covered with a monolayer of PS nanospheres. We do observe areas where multilayers of PS nanospheres were formed. Such areas were excluded in our experimental analysis. The sample was then etched in a Reactive Ion Etching (RIE) system in oxygen plasma (O₂ flow 20sccm, pressure 15mTorr, RF power 100W). The system used was Plasmalab80Plus from Oxford Instruments. The RIE process reduced the nanosphere size and while simultaneously hardened the PS, transforming the PS nanospheres into a negative mask for the next etch step.

Figure 4.2. SEM images of the SiO₂ nanodisks-patterned substrate: (a) top view, (b) 45° oblique view.

The SiO₂ layer was anisotropically etched by using the RIE system previously used. The gases were 25sccm of CHF₃ flow and 25 sccm of Ar. The pressure was 30mTorr

and RF power was 150W. After etching, the monolayer mask resulted in an array of SiO₂ nanodisks arranged in a hexagonal close packed lattice. Finally, the PS nanospheres were removed by immersing the sample in toluene in an ultrasonic bath, leaving the SiO₂ nanodisk array on the GaAs substrate. The final pattern is shown in Fig. 4.2, where the SiO₂ nanodisk is of 210nm in diameter, 60nm in height, and hexagonally arranged with periodicity of 280nm on top of GaAs (100) substrate.

We observe three types of arrangement defects in the PS nanosphere array. At the lowest length scale, the defect type observed is vacancy defect where a PS nanosphere is missing from a lattice site. At longer length scale, another type of defect is observed where PS nanosphere arrays seem to form “grain boundaries”, i.e. the PS nanosphere arrays form different groups, each with different lattice orientation. The average size of the “grain”, or the extent to which the PS nanospheres are arranged uniformly until they meet another group of different orientation, is measured as correlation length. Mathematically, the correlation length can be obtained from the size of spots in the Fourier Transform image of the PS nanosphere array. In our case, the correlation length is measured to be ~12μm.

At even longer length scale, and perhaps the most important defect type for our case, there is bilayering problem. As mentioned earlier, we also observed multi-layer of PS nanospheres on the substrate, mostly is bilayer. Etching through bilayer PS nanospheres will result in triangular openings on the SiO₂ layer. The triangular opening areas are observed to be immediately adjacent to the nanodisk area, which results from monolayer PS nanosphere array (see Fig. 4.3). During growth, the triangular opening area will absorb adatom flux by a different amount from the

nanodisk area. This difference is not desirable as it reduces the degree of tunability of island height. The incoming adatom flux and the nanodisk coverage are directly related to the expected island height.

Figure 4.3. Nanodisk area and triangular opening area adjacent to each other.

In order to avoid this problem, we have attempted to exclude the multilayer area altogether by using a different PS nanosphere layering method, which will be elaborated in Section 4.1.2 below.

4.1.2 Colloidal method to self-assemble PS nanospheres

The multilayering of PS nanospheres in the previous section is related to the surface tension of water which hosts the PS nanospheres. High surface tension implies high contact angle, which further suggests more tendency for agglomeration. This

problem can be overcome by forcing the PS nanospheres to assemble on the water surface with the aid of surface tension, and by adding surfactant in order to reduce the surface tension so as to increase the wettability of PS nanospheres on the water surface. The PS layering was done by colleagues from School of Materials Science and Engineering (MSE) in the same university which is based on the work in Ref. 2.

The outline of the method is schematically drawn in Fig. 4.4, which is briefly explained in the following steps. One piece of piranha-cleaned glass slide was placed in the center of a petri dish. DI water was added into the dish to a level where a convex meniscus was formed at the boundary of the glass slide [Fig. 4.4(a)]. PS solution was dropped by a pipette on the glass slide [Fig. 4.4(b)]. PS nanospheres would spread on the water surface rapidly [Fig. 4.4(c)] and self-assemble into ordered monolayer once the PS suspension on the glass slide met the surrounding DI water [Fig. 4.4(d)]. To consolidate the monolayer, 20 μL of 2 wt % dodecylsodiumsulfate (SDS) solution was added to the system to further reduce the surface tension. DI water was then added again to raise the liquid level [Fig. 4.4(e)]. Finally, the monolayer was fished out by the substrate and the sample was dried by natural evaporation at room temperature [Fig. 4.4(f)]. The resulting PS monolayer arranged on a substrate is shown in Fig. 4.5. In this method, the possibility of forming bilayer PS nanospheres is theoretically zeroed by virtue of the contact angle of the surfactant. The contact angle of the surfactant limits the number of PS nanosphere layers which can float on the air-water interface. Using this method, areas in the order of cm^2 size of close-packed PS monolayer has been demonstrated. No bilayer PS nanosphere array is observed on the sample. However, vacancy defect and “grain boundaries” can still be seen. The correlation length is measured to be

~15 μm . The increase in correlation length compared to that of the earlier spin-coated PS nanosphere array signifies an improvement in the arrangement.

Figure 4.4. The schematic of colloidal technique as outlined in Ref. 2.

Similar process steps as those for the earlier SiO₂ nanodisk-patterned substrate were then applied to the sample. This time, due to resource constraint the dry etching was performed by the use of AST Clen100 which is typically used for descum purposes. The drawback of AST Clen100 is that the pressure cannot be independently controlled. Thus, the gas flows have to be tuned in order to obtain a low pressure. Based on our observation, it is found that the pressure is almost linearly correlated with the total gas flow involved in the etching. An O₂ plasma treatment (O₂ flow: 20sccm, RF power: 60W, pressure 168 mTorr) was used to reduce the size of the nanodisk.

Figure 4.5. PS nanosphere array formed by colloidal method, arranged on SiO_2 layer on GaAs substrate.

Figure 4.6. The final PS diameter as a function of O_2 plasma treatment duration.

The measurement of the average PS diameter as a function of the duration of oxygen plasma treatment is shown in Fig. 4.6. The measurements of a large array of PS nanospheres were obtained from SEM imaging, which was then exported for image processing. By the use of contrast threshold in the image processing, it is possible to

acquire feret diameter of each PS nanosphere, which was then put into histogram in order to deduce the average diameter. It is observed that the final PS diameter seems to saturate at 50nm. This is probably because of the completely crosslinked PS nanospheres after more than 60s oxygen plasma treatment.

Figure 4.7. PS nanosphere array after 20 seconds of O₂ plasma treatment.

The example of PS nanospheres subjected to 20s oxygen plasma treatment is shown in Fig. 4.7. Here, the PS diameter is reduced from 285nm (i.e., when $t=0$ s) to about 250nm. Afterwards the SiO₂ layer underneath the PS nanospheres was etched down by CF₄/O₂ gas system by using the same machine. First, we characterized the etch rate of a planar SiO₂ layer which was deposited in the same condition as the SiO₂ layer underneath the nanospheres. We varied the ratio of CF₄ and O₂ flow, while characterizing the pressure at the same time. The SiO₂ samples were then etched for 10 minutes and characterized by surface profiler. The relationship between the pressure, etch rate, and gas composition is shown in Fig. 4.8. The RF power was fixed to 100W.

Figure 4.8. (a) The pressure as a function of total gas flow. (b) the etch rate as a function of pressure.

It can be observed that the linear relationship between the pressure and the total gas flow is apparent [Fig. 4.8(a)]. The etch rate of SiO₂ planar layer has been optimized up to 63nm/min when CF₄ flow is 5sccm and O₂ is 5sccm. However, because PS nanospheres also react with oxygen plasma, it is instructive to decrease the fraction of O₂ relative to CF₄ gases so that most of the etching occurs in SiO₂, instead of PS. Thus, 5sccm O₂ and 50sccm CF₄ was chosen for our purposes, which exhibited the

etch rate of 26nm/min on a planar SiO₂ layer. The result after O₂ plasma treatment and SiO₂ etching is shown in Fig. 4.9(a). After the SiO₂ etching, we have also removed the PS nanospheres by dissolution in DI water, and the result is shown in Fig. 4.9(b).

Figure 4.9. (a) PS nanosphere array after CF₄/O₂ dry etch; (b) the resulting SiO₂ nanodisks after the PS nanospheres were removed.

During the SEM observation of the SiO₂ nanodisks, the sample suffered from severe charging, suggesting the existence of SiO₂ residual layer, despite the fact that we have overestimated the etching time to ensure that the etching process reaches the interface between SiO₂ and GaAs. This is probably because of the loading effect in etching, where narrower opening gives lower etching rate. It is also observed that after the SiO₂ etching, there was some scum on the sample, which remained even after an additional 1 minute descum step. Further investigations are needed, and in the future, growth on this SiO₂ nanodisk-patterned substrate shows the potential to show even more uniform islands than that of the earlier substrate which was patterned by spin-coating.

4.2 Hydrogen silsesquioxane-based Patterned Substrate

In the previous two sections, we have explored the patterning of SiO₂ nanodisks by means of nanosphere lithography, based on spin coating and colloidal method. This method has inherent weaknesses in that the positions of silica nanodisk cannot be independently determined (e.g. limited to hexagonal arrangement) and the roughness is inevitable as a result of dry etching. In this and the following section, we explored the use of electron beam lithography. Hydrogen silsesquioxane (HSQ) was used as the e-beam resist. HSQ is a high resolution negative tone electron beam resist which upon exposure by electron beam will turn into a compound which is compositionally close to SiO₂ (SiO_x), which is similar to the composition of SiO₂ nanodisk discussed in the previous section. As will be explained later in Chapter 5, it is reasonable to hypothesize that SiO_x is the catalyst responsible for the catalytic growth. Therefore we exposed patterns of differing shapes on HSQ with the aim to demonstrate

catalytic growth. Compared to the process described in Section 4.1 earlier, this process line is simpler because no etching is required. The process line is described schematically in Fig. 4.10.

Figure 4.10. Schematic of process line to realize HSQ nanodisks on GaAs substrate.

We first attempted to pattern an array of nanodisks of differing size and spacing on GaAs substrate. The HSQ resist used was XR-1541-006 from Dow Corning Corp. The resist was spin-coated at 4500rpm for 60s, resulting in 85nm resist thickness. After running a series of dose test, the area dose was set to be approximately 1000 $\mu\text{C}/\text{cm}^2$. The dwell time for a given area dose, i.e., the duration of the electron beam dwelling in one position, was calculated by measuring the current in Faraday cup and by assuming the pixel size of 20nm x 20nm. Then, the dwell time was used to determine the dot dose which was extensively used in our pattern definition. The electron energy (EHT) and the electron beam aperture were set to 20kV and 20 μm , respectively. The measured current for the given EHT and aperture size was about 0.153nA. In addition to dose, the way the pattern is drawn in the mask file apparently has an effect to the final pattern after development. We observed that patterns generated based on two dimensional area in the layout tended to stick less with the substrate compared to those generated based on series of concentric lines and vertices. This may be caused by more annealing effects on resist-substrate interface

when the pattern is written in concentric fashion rather than line-by-line fashion. The writing strategy of various shapes based on concentric lines is schematically illustrated in Fig. 4.11.

Figure 4.11. The writing strategy of four distinct shapes in nanopatterning based on concentric lines.

Here, the concentric lines and arcs are separated by 10-20nm because we adopt the assumption that the beam spot size of the electron beam is about 10-20nm. The number of vertices in writing arc structure is crucial as it ensures the continuity (smoothness) of the resulting arc after development. In this case, we defined 32 vertices for every circular arc in the pattern. After exposure the sample was immersed in trimethyl-ammonium-hydroxide (TMAH) solution (10% in water) for 1 minute and rinsed in DI water. Upon SEM inspection, it was found that most of the disk patterns that were written as two-dimensional areas disappeared, and the ones that remained on the substrate did not form a perfect circle and arranged in rather arbitrary pattern. On other hand, the patterns written as series of concentric arcs survived albeit with arbitrary arrangement [Fig. 4.12(a)].

Therefore the disks resulting from concentric arcs tended to stick better to the substrate compared to the ones resulting from two-dimensional area written in FBMS mode, as explained earlier. The faint dots inside the nanodisks are the traces of the electron beam spot [Fig. 4.12(b)]. The number of the faint dots is exactly the same as the number of vertices defined in the mask layout. In the subsequent experiment, we have increased the number of vertices to smoothen out the dose throughout the nanodisk. The black circle in the centre of the nanodisk can be avoided by drawing an additional dot at the center of the concentric arc patterns (see Fig. 4.11). In addition, we also observed residual HSQ layer surrounding the nanodisk in Fig. 4.12(b). After series of dose test, we deduced that the HSQ dose-to-clear is larger than $700 \mu\text{C}/\text{cm}^2$. This suggests that the HSQ residual layer is not caused by underexposure of e-beam, but rather due to rinsing method after development.

There are two aspects which we believe are related to adhesion properties: (1) the chemistry of two materials (HSQ resist and GaAs substrate) which determines the contact angle between them, and (2) the pattern aspect ratio. The chemistry of the two materials cannot be changed, so the contact angle problem is rather inevitable. However, it is possible to decrease the resist thickness, for example by diluting HSQ in methyl-isobutyl-ketone (MIBK) solution. To solve the adhesion problem, we first factored out the 1st aspect by creating the patterns on Si substrate instead, since HSQ has better adhesion properties with Si. The reason is because Si and amorphous silica (SiO_x) both have Si as the common element, so they stick well to each other. The resist thickness was fixed to 85nm. The sample was again developed in TMAH 10% solution for 1 minute, with modified rinsing strategy by using flowing DI water onto the sample for 30s. The number of vertices in the circular arc in the pattern was

increased from 32 to 128 in order to ensure pattern continuity. The pattern consisting of arrays of decreasing disk diameter, periodic array of single size disks, and arrays of variable shapes and sizes are shown in Fig. 4.13, 4.14, and 4.15, respectively.

Figure 4.12. SiO_x nanodisks on GaAs substrate: (a) various diameters; (b) zoomed-in view to one of the nanodisk, showing traces of ~10nm sized beam spots.

Figure 4.13. SiO_x nanodisks of differing sizes on Si substrate: (a) lower magnification view to show the arrangement; (b) higher magnification view to show the size and resist thickness.

By comparing Fig. 4.13, 4.14, and 4.15, it is observed that circular patterns tend to stick better compared to the non-circular ones. The measurement of circular patterns shows that the patterns are larger by 10-20nm compared to originally designed

dimensions. This is primarily caused by the divergence angle of the e-beam as a result of forward scattering of electrons in the resist. Fig. 4.13(b) shows the case when the smallest SiO_x pillar topples down. SEM measurement of the toppled nano pillars show that the average height of the toppled pillar to be $\sim 80\text{nm}$, confirming the 85nm thickness of HSQ resist spun coat earlier. Thus, the divergence angle of the e-beam [see Fig. 4.13(b)] can be deduced with the help of top width and base width of the toppled nano pillar as $\theta = \tan^{-1}[(79.55 - 47.78)/(2 \times 80)] \cong 11.2^\circ$. Such a diverging structure makes circular patterns to be the most stable in comparison with the non-circular ones. This is also confirmed in the array of periodic single size nanodisks in Fig. 4.14.

Figure 4.14. Periodic array of single size SiO_x nanodisks on Si substrate.

The reason that smaller nanodisk topples in Fig. 4.13 can be explained from the fact that smaller disks have higher aspect ratio, therefore they are more unstable

compared to the larger ones. In addition, the non-circular patterns are written based on areas rather than concentric lines. Note that the above adhesion problem occurs on Si substrate which has good adhesion properties with HSQ, thus the method to solve the above adhesion problem should be purely geometrical in this case.

Figure 4.15. Various shapes and sizes of SiO_x nanostructures on Si substrate. The pattern writing method is based on area drawing.

For that reason, we then attempted to thin down the HSQ resist using its solvent which is MIBK (methylisobutylketone). The dilution ratio is 1:1. Surface profiler measurement shows that spin-coating HSQ:MIBK=1:1 on Si substrate at 4000rpm for 60s resulted in 42nm-thick HSQ resist, which is about 2 times thinner than the original HSQ resist. This is to be expected since the concentration is reduced by a factor of 2.

Figure 4.16. SiO_x nanodisks resulting from exposing diluted HSQ: (a) lower magnification view to show the periodic arrangement; (b) higher magnification view to show the size of the nanodisks.

A series of dose tests in diluted HSQ resist indicate that the e-beam dose remains unchanged compared to the previous HSQ resist. More diameter variations down to

20nm have been incorporated in the mask. In order to reduce the divergence angle of the e-beam, the SEM aperture was decreased from 20 μ m to 10 μ m, while keeping the EHT to 20kV. The measured current was 0.045nA, which was 4x lower compared to that of 20 μ m aperture size. This is to be expected, since the current is linearly proportional to the aperture area. Alternatively, e-beam divergence angle can be decreased by increasing the working distance, which translates into a longer depth of focus of the e-beam. However, this comes at the expense of a decrease in e-beam resolution. In the context of this work, we did not change the working distance. The developed HSQ sample is shown in Fig. 4.16.

It was observed that patterns with sizes down to 20nm have been demonstrated in the area spanning over few mm². Here, we have also modified the rectangular and triangular patterns to be based on concentric lines. The resulting patterns no longer have adhesion problem. This is shown in Fig. 4.17, where the pattern consists of squares, triangles, rings with differing sizes from 100nm down to 20nm in 3 x 4 arrays, which is repeated every 2 μ m in x and y directions.

The patterns on the first row in Fig. 4.17(b) were designed as single line exposure. The designed patterns are in the form of a rectangle (first structure from left), a triangle (second structure from left), a ring (third structure from left) with the size or diameter of 50nm. Additionally, we also designed a very small ring of 20nm diameter as demonstrated in the fourth structure. The resulting rectangle width is 53nm, and the hole in the center of the rectangle is measured to be 17nm. The outer ring diameter is 76nm with the inner hole diameter of 42nm. The linewidth of the e-beam line exposure was measured to be 16nm. The fourth structure is reduced to a

point-like structure with 40nm diameter, which is consistent with size of the e-beam linewidth. This is also similar with the very small triangular disk in the middle far right in Fig. 4.17, which has the size of 24nm.

Figure 4.17. (a) Arrays of rectangles, triangles, and rings exposed on 42nm-thick HSQ resist, (b) higher magnification view and measurements of some of the patterns.

Indeed, the above results show a great potential in creating quantum dot in tunable sizes and shapes, when the above SiO_x nanodisks are used as a template to catalytically grow islands (as will be explained further in Chapter 5). The adhesion problem between GaAs and HSQ resist can be mitigated by depositing a very thin layer of SiO_2 film, with thickness falling in the range of 10-20nm, before spin-coating HSQ resist. Since both layers have silicon in their composition, adhesion properties between them should be better, just like the case of HSQ on Si. Furthermore, by annealing the exposed HSQ in hydrogen environment it is possible to tune the nonstoichiometricity of the SiO_x material [3]. The degree of nonstoichiometricity might be used to tune the catalytic strength of the SiO_x , thus adding another tunable parameter to the growth process.

4.3 Gold Nanodisk-based Patterned Substrate

Gold (Au) has been commonly used as catalyst in growing GaAs nanowires by Vapor-Liquid-Solid (VLS) method. It is therefore reasonable to use Au as the catalyst to grow GaAs islands on GaAs(100) substrate and investigate whether the catalytic and faceting phenomenon can be realized. The important difference between our growth mechanism and VLS mechanism is that the substrate used in our case is of (100) orientation, whereas for VLS nanowire growth, (111) substrate is mostly used. Growth rate at (111) orientation is preferred to growth at other planes, rendering the growth rate to be very fast, resulting in high aspect ratio nanowires. However for our case, we would like to combine catalytic effect and faceting mechanism to form a pyramidal island. Faceting mechanism serves as a limiting force such that the growth is not self-sustaining like in the case of nanowire growth.

In this case, two positive tone resists are explored, namely; PMMA A2 with 950K molecular weight (from MicroChem) and ZEP520A-7 (from Zeon Corp.). The process line to fabricate gold patterns on GaAs (100) substrate based on both resists is described schematically in Fig. 4.18.

In most of nanopatterning cases, thin resist is often required in order to produce a high resolution sub-50nm patterns. In this case, we first explored PMMA A2 since it has good adhesion properties with almost all material and that it can be deposited with thickness down to 50nm when spin-coated at 4000rpm for 60s. The dose-to-clear for PMMA is well known to be around $200\mu\text{C}/\text{cm}^2$ with 20kV EHT. This may not apply in our case, since typically high dose is required to ensure the e-beam to penetrate sufficiently deep in that all the PMMA is exposed. However, in thin resist the dose-to-clear may be lower than $200\mu\text{C}/\text{cm}^2$.

Figure 4.18. Schematic of process line to realize gold nanodisks pattern on GaAs substrate: (a) spin coat ZEP/PMMA resist, followed by e-beam exposure; (b) develop ZEP/PMMA to reveal the holes on the ZEP/PMMA resist; (c) evaporate Au; (d) lift-off, leaving Au on the substrate.

To verify this, we did a preliminary test where we spin coated 200nm thick PMMA and exposed it with $300 \times 300 \mu\text{m}^2$ boxes with dose ranging from $50 \mu\text{C}/\text{cm}^2$ to $200 \mu\text{C}/\text{cm}^2$. After developing in MIBK:IPA=1:3 for 60s and rinsing in IPA for 30s, the remaining PMMA thickness of each box was deduced by a reflectometer (NanoCalc from Micropack), which has sensitivity down to 10nm. The measurement of e-beam penetration depth as a function of e-beam dose is shown in Fig. 4.19. It is evident that for PMMA A2 with 50nm film thickness, an area dose of around $70 \mu\text{C}/\text{cm}^2$ is sufficient, instead of $200 \mu\text{C}/\text{cm}^2$. Such a reduced dose is crucial for mitigating e-beam proximity effects in nanopatterning. The same pattern as those in the previous section was written on PMMA A2, which then was followed by e-beam evaporation of gold. To have a successful lift-off, it is important to ensure the structures to have a good undercut profile, followed by the metal thickness not exceeding one third of the resist thickness. In our experiment, we evaporated 12nm of gold on developed 50nm-thick PMMA film with e-beam dose around $70 \mu\text{C}/\text{cm}^2$. Lift-off was carried out by soaking the sample inside acetone.

Figure 4.19. The e-beam penetration depth vs e-beam dose in 200nm PMMA film.

It was found that the lift-off was unsuccessful as the PMMA was not dissolved in acetone. Indeed, a signature of crosslinking during e-beam evaporation was apparent. Despite the fact that temperature was indicated as below 40°C at the finish of e-beam evaporation, it should be noted that evaporated atoms inherently have temperature in thousands of degrees range. Apparently, a 50nm-thick PMMA film was not strong enough to withstand the flow of heat from evaporated atoms. We changed the deposition rate so as to slow down the heat flow from evaporated atoms down to 0.01nm/s, however the same PMMA crosslinking was still observed. Fig. 4.20 shows the SEM picture of the crosslinked film, and it can be seen that nanocracks in PMMA film is evident.

Figure 4.20. The existence of nanocracks due to film crosslinking.

Despite the fact that ~50nm feature sizes have been successfully patterned in PMMA A2 film, the constraint of film thickness makes it challenging in lift-process process. Indeed, it is possible to pattern sub-50nm features in thicker resist, however, that

requires e-beam lithography system with 100kV EHT, e.g., JEOL system, which is not available in our place.

Therefore, we turned to ZEP520A-7 resist. Despite the fact that thickness of ZEP520A-7 is of the order of 200nm, it should be noted that ZEP is a chemically amplified resist, which means the dose can be much lower compared to PMMA, while at the same time, has stronger resistance to dry etching. The ZEP was spin coated on the GaAs substrate at 4000rpm speed for 60s, giving 200nm resist thickness. Similarly to previous EBL process lines, a series of dose tests is performed to obtain e-beam clearing dose, which was found to be $> 30\mu\text{C}/\text{cm}^2$. After exposure, the sample was immersed in N-amyl acetate for 30s, followed by rinsing in MIBK:IPA=89:11 solution for another 30s. Afterwards Au was evaporated into the holes using Electron Beam Evaporator and lift-off was performed by soaking the sample in dimethylacetamide with slight sonication. The lift-off was unsuccessful, this time the reason was not because of crosslinking, but we found that Au did not stick to the GaAs substrate and preferred to form a layer with the Au part outside the intended patterns. As a result, after lift off, both the metal and the resist were removed.

To overcome this problem, we have evaporated a thin layer of titanium (Ti) before evaporating Au. It is well-known that Ti improves adhesion of Au to GaAs substrate. Here, the e-beam dose was varied from $30\mu\text{C}/\text{cm}^2$ to $48\mu\text{C}/\text{cm}^2$, followed with e-beam evaporation with 2nm Ti and 20nm Au. Fig. 4.21 shows the resulting 60nm diameter Ti-Au nanodisks for $30\mu\text{C}/\text{cm}^2$ e-beam dose.

Figure 4.21. Sub-100nm Ti/Au metal patterning. The e-beam dose, EHT, and aperture size were $30\mu\text{C}/\text{cm}^2$, 20kV and 20 μm , respectively.

It can be seen that the resulting metal disk is inherently elongated and rather slanted by 45° angle. From the slant angle, it is evident that the sample was rather misaligned during the e-beam evaporation process. This is further verified with the fact that the vertical dimension of the metal disk is $\sim 62\text{nm}$ (see Fig. 4.21), which is almost similar to designed dimension, i.e., 60nm. It should be noted that the oblique evaporation angle only affects the angle of the final patterns, and it does not change the final size provided the undercut profile is more than the evaporation conical angle. One can have reasonable estimates of the conical evaporation half-angle (which is not the oblique evaporation angle) by $\theta = \tan^{-1}[(80.35 - 62.23)/(2 \times 200)] \cong 2.6^\circ$, for the 200nm resist thickness and 60nm nominal (designed) pattern.

Figure 4.22. The closely spaced and decreasing size Ti/Au nanodisks.

This is consistent with the earlier measures of e-beam diverging half-angle of $\sim 11.2^\circ$, because this signifies the estimate angle of the undercut profile in the ZEP resist after developing. Note that the estimated undercut angle is reasonable since the required e-beam dose for ZEP film is considered low. In addition, because the e-beam diverging angle is larger than the e-beam evaporation angle, this also suggests that there was no metal deposition on the ZEP sidewall, thus confirming the fact that the oblique evaporation angle does not affect the final metal size. The patterns with differing disk diameters are shown in Fig. 4.22 for the same e-beam dose. Clearly, the aspect of proximity effect together with oblique evaporation is clearly seen, where the gap separations between the patterns generally decrease and the last two patterns overlapped. Increasing the e-beam dose would naturally give rise to larger metal dimensions. This is illustrated in Fig. 4.23 where the e-beam dose is increased to $40\mu\text{C}/\text{cm}^2$, where the size has increased as much as 10nm. For the non-circular structures, the patterns for $30\mu\text{C}/\text{cm}^2$ and $40\mu\text{C}/\text{cm}^2$ dose were not completely formed. This is because in the e-beam evaporation with certain conical angle (which

is $\theta \sim 5^\circ$ according to the previous estimation), the evaporated atoms tend to join with each other rather than going through the narrow openings defined by the EBL.

Figure 4.23. The result of patterning 60nm-diameter two dimensional disk patterns for e-beam dose of $40\mu\text{C}/\text{cm}^2$.

Figure 4.24. Noncircular metal disks for different e-beam doses.

In order to verify this reasoning, the SEM images of the same non-circular structures for the dose of $30\mu\text{C}/\text{cm}^2$, $40\mu\text{C}/\text{cm}^2$, and $48\mu\text{C}/\text{cm}^2$ are plotted side by side in Fig. 4.24. The rather distorted rectangles and triangles are to be expected since the evaporation is rather misaligned. We can see that the patterns become more completely formed when the e-beam dose is increased. Finally, measurement of the

non-circular patterns for e-beam dose of $48\mu\text{C}/\text{cm}^2$ is shown in Fig. 4.25. It can be seen that despite the apparent distortion in the pattern, clearly a metal structure with the size ranging from 23nm to 153nm can be obtained by this lift-off method. We observed that this lift-off method is repeatable throughout a large area where all the patterns are defined. Indeed, this shows the remarkable pattern fidelity in this method, similar to HSQ pattern in the previous section. Therefore, patterning of sub-50nm metals is a reasonable direction for future research and it has a great potential to be used as the template for metal-based catalytic island growth. We also have shown that it is possible to achieve much smaller pattern dimension ($\sim 20\text{nm}$) despite the thickness of the resist (200nm). Of course, the proximity effects demonstrated in Fig. 4.22 can be further mitigated by decreasing the aperture size so as to reduce the undercut angles or by slightly decrease resist thickness.

Figure 4.25. Measurements of non-circular structures for $48\mu\text{C}/\text{cm}^2$ e-beam dose.

One can have alternative method which is not based on lift-off technique. Nano metal patterning can also be realized by the use of surface functionalization for attracting

specific metals. Notable examples are amino-silane adhesion agent such as 3-(2-aminoethylamino) propyltrimethoxysilane [4] or 3-aminopropyltriethoxysilane (APTES) that specifically binds gold particles. The dangling bonds of the amino-silane compound serve as the connecting bridge, or “glue”, between GaAs and Au. Using this method, metal evaporation is no longer necessary and one can use gold colloidal solution instead. Thus, this serves as the low temperature version of metal nano patterning described previously. First, the sample is exposed by electron beam lithography, which is then followed by spin coating amino-silane agent in order to functionalize the surface. Afterwards, the gold colloidal solution is dispensed on the sample, which then followed by removal of e-beam resists, leaving gold nanoparticles exactly localized within the opening that were previously patterned by the EBL. However, it should be noted that such an advantage comes with a drawback, because the presence of amino-silane adhesive gives organic contamination inside growth chamber. Thus, this approach is only feasible for MOCVD because organic materials are permitted inside the chamber.

4.4 Summary

In this chapter, we have reviewed external patterning methods based on nanosphere lithography and electron beam lithography, to demonstrate island growth based on catalytic growth and facet formation. For nanosphere lithography, we have attempted two types of PS nanosphere layering methods, one was based on spin-coating, the other was based on colloidal method. For electron beam lithography patterning, we have achieved sub-50nm SiO_x and Ti-Au nanostructures of differing shapes. In the next chapter, we will see how nanosphere lithography works together with catalytic growth and facet formation to form islands of uniform size, shape and arrangement.

Chapter 5: Results and Discussion

In this chapter we will elaborate on the growth results on nanodisk-based patterned substrate which were fabricated in Institute of Materials Research and Engineering, Singapore using PS spin-coating method, as elaborated in Section 4.1.1 earlier. We will discuss the various aspects of the grown islands, e.g. the growth mechanism, uniformity, and composition.

5.1 Growth Conditions

Prior to growth, the patterned substrate was immersed in dilute $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solution for one minute, to provide a clean and ready epitaxial surface. The substrate were then loaded into the MBE system and pre-heated in the transfer chamber up to 500°C to remove moisture and other contamination. GaAs was then grown on the patterned sample using a Solid Source Molecular Beam Epitaxy (SSMBE) with growth rate of 0.1ML/s at substrate temperature of 630°C . These growth conditions were adapted from work reported by Lee et al. [1]. Using these conditions, the adatoms were encouraged to arrange in relation to the patterns on the substrate. High growth temperature imparts high kinetic energy to the adatoms, which implies that the adatoms have longer diffusion length in higher temperature. Thus, the adatoms are able to “explore” more areas, allowing them to be exposed to the effect of the patterns on the substrate. The high kinetic energy also gives the adatoms extra energy to overcome unwanted potential barriers such as roughness on the substrate. Low growth rate promotes unhindered adatom movement, preventing adatoms from

coalescing before reaching the intended location.

The amount of material grown is varied across samples and the parameter used to quantify the material is nominal deposition thickness. The term “nominal” here refers to the equivalent deposition thickness when GaAs is deposited on a planar unpatterned surface. The nominal deposition thickness is set to 5nm, 10nm, and 20nm.

5.2 Growth Mechanism

The as-grown samples are imaged with SEM as shown in Fig. 5.1. For ease of discussion, the samples are labeled according to its nominal deposition thickness, e.g. 5nm-sample refers to the sample grown with 5nm nominal deposition thickness. From the top view, 5nm-sample seems not to have any growth at all [Fig. 5.1(a)]. However for 10nm-sample, there are islands growing from underneath the SiO₂ nanodisk and some have even toppled the SiO₂ nanodisk over [Fig. 5.1(b)]. Some of the nanodisks are seen to have been dislocated from their original positions. The islands, on the other hand, maintain their periodicity. Similar case happens for 20-nm sample [Fig. 5.1(c)], and there are even islands who have freed themselves completely from the nanodisks. Oblique and higher magnification SEM views confirm these observations and add more perspective: the island growth from underneath the SiO₂ nanodisk has also happened in 5nm-sample [Fig. 5.1(d)]. For 5nm-sample [Fig. 5.1(a)], the island seems to have pushed up the SiO₂ nanodisk. This is somewhat similar to the commonly observed gold particle catalyst being lifted up in Vapor-Liquid-Solid (VLS) nanowire growth [2, 3]. If we compare Fig. 5.1(e) and Fig. 5.1(f), the 20nm-islands seem to be taller than 10nm-islands.

This growth mode is entirely different from the commonly known SiO_2 masking function in selective growth. Instead of growing outside the SiO_2 region, the GaAs has grown “within” the SiO_2 region.

Figure 5.1. Island growth and its evolution as nominal deposition thickness is varied across samples as: (a) 5nm; (b) 10nm; (c) 20nm; (d)-(f): oblique and higher magnification view of 5nm-, 10nm-, and 20nm-islands, respectively.

To fully reveal the islands, the samples are dipped into HF solution, and the result is shown in Fig. 5.2. The SiO_2 nanodisks are thoroughly etched away by HF, leaving the islands behind, therefore suggesting that the island composition is highly likely to be GaAs. After nanodisk removal [Fig. 5.2(a) and 5.2(d)], expectantly, the top part of

the 5nm-island is revealed to be a plateau. This suggests that the growth must have started simultaneously from all points on the SiO₂-GaAs interface and proceeding at the same rate, which is an indicative of “catalytic” growth. The sidewalls of the 5nm-islands are observed to be rather sloped, which may indicate an early stage of facet formation.

Figure 5.2. After nanodisk removal: (a) 5nm-; (b) 10nm-; (c) 20nm-sample; (d)-(f): oblique and higher magnification view of 5nm-, 10nm-, and 20nm-sample, respectively.

At 10nm-sample [Fig. 5.2(e)], it is observed that the islands have grown into a pyramidal shape, giving additional evidence of facet formation during the growth

process. In the shape evolution from plateau [Fig. 5.2(d)] to pyramidal [Fig. 5.2(e)], it is clear that the interfacial area between SiO_2 and GaAs island decreases as the facet formation progresses. At this stage, it is reasonable to suppose that the SiO_2 nanodisk on top of the island starts to tilt on its centre and eventually is toppled over. The same phenomenon happens when the nominal deposition thickness is set to 20nm [Fig. 5.2(c)], however the facets of the 20nm-islands are more developed than those of 10nm-islands [Fig. 5.2(e)], and this is also evident from the edge effects observed in the top-view SEM image of the 20nm-islands in Fig. 5.2(c).

Faceted GaAs islands on patterned GaAs substrates have been demonstrated for example in Ref. 4, where the faceted GaAs islands grew inside SiO_2 mask openings. The faceting originates from minimization of surface energy to achieve the most equilibrium crystal shape.

5.3 Island Composition

The XRD spectra of as-grown 20nm-islands is presented in Fig. 5.3 to give an additional verification on the island material composition, showing that only GaAs signals exist, represented by GaAs(002) and GaAs(004) peaks. Since the islands are faceted, it is highly likely that the islands are crystalline GaAs.

Figure 5.3. XRD spectra of as-grown 20nm-islands.

5.4 Uniformity in Arrangement

The growth phenomenon happens consistently throughout a large area of $\sim 50 \times 50 \mu\text{m}^2$ range. However, due to space constraint, only the SEM image of $\sim 10 \mu\text{m} \times 10 \mu\text{m}$ area is shown here for 20nm-islands [Fig. 5.4(a)]. The island geometrical arrangement can be deduced by calculating the Fourier Transform (FT) of the SEM image, with DC component removed. As shown in Fig. 5.4 (b), the FT image has 6 clusters of spots, each of which consists of 4 bright spots. The 6 clusters are spaced out in hexagonal manner, corresponding to the triangular lattice periodicity of the islands, while the 4 spots signify 4 different orientations of blocks of triangular lattice-arranged islands (i.e., “grain boundaries”), marked by boundary lines and colored arrows in Fig. 5.4 (a). These “grain boundaries” originate from the non-uniformity of PS nanosphere locations during spin coating process in the nanosphere lithography, as has been mentioned in Chapter 4, section 4.1 earlier. The periodicity of the islands can be deduced from the annular radius of the FT image, giving the

period of 283nm, and in a good agreement with that of SiO₂ nanodisks, which is 280nm.

Figure 5.4. (a) Top view SEM image of 20nm-islands after SiO₂ nanodisk removal, showing ordered arrangement of the islands over ~10μm x 10μm area; (b) Fourier Transform of the SEM image, with DC component filtered.

5.5 Uniformity in Size

Next, the uniformity of the SiO₂ nanodisks and the GaAs islands are quantified by image processing of the SEM images. We applied a threshold to the image brightness, such that the lowest brightness coincides with the nanodisk/island base. After threshold is applied, the image comprises of new objects which are the disks/islands

without background substrate information. Measurements are then applied on these new objects. The lateral size of the SiO₂ nanodisks and islands is represented by a term called feret diameter, defined as the longest point-to-point distance in the periphery of an object. This parameter is chosen because of the different shapes of the base of the nanodisks and islands, i.e., the nanodisks and 5nm-islands having circular shape whereas 10nm- and 20nm-islands, quadrilateral shape.

Figure 5.5. Lateral size distribution of: (a) SiO₂ nanodisks; (b) 5nm-islands; (c) 10nm-islands; (d) 20nm-islands. The insets show the SEM images of the respective nanodisk or island.

Fig. 5.5 presents the lateral size distribution of the nanodisks and the islands in histogram plot, where the lateral size uniformity of each case is characterized by the parameter δ , which is the standard deviation (σ_d) normalized to the mean feret diameter (μ_d) of the islands.

$$\delta = \sigma_d / \mu_d \quad (5.1)$$

The detailed statistical data of the nanodisks and islands are shown in Table 5.1, where the term “counts” represents the number of nanodisks or islands used in the statistical analysis.

	nanodisks	5nm-islands	10nm-islands	20nm-islands
σ_d (nm)	210.51	239.66	179.56	220.85
μ_d (nm)	12.07	15.68	25.03	19.29
δ (%)	5.74	6.54	13.94	8.74
counts	907	281	288	265

Table 5.1. Statistical data of the lateral size of the nanodisks, 5nm-islands, 10nm-islands, and 20nm-islands.

During the pattern transfer from SiO₂ nanodisk to 5nm islands, δ changes from 5.74% to 6.54%. At this stage, the uniformity is still relatively preserved because the island shape still follows the shape of the SiO₂ nanodisk, and the facet formation is still in its early stage. However, as the nominal deposition thickness is increased to 10nm and 20nm, we have a situation in which the δ increases to 13.94% (for 10nm case) and decreases back to 8.74% (for 20nm case). Such a difference in δ is an indicative of island base shape transformation from circular (i.e., in 5nm case) to quadrilateral (i.e., in 20nm case), where the 10nm case is probably near the transition stage between these two shapes. This can be explained when one considers lateral adatom adsorption, as resulted from lateral movement of adatoms. In 5nm case, the island growth is still dominated by “catalytic” mechanism in the vertical direction, with the rate dependent on the interfacial area between GaAs and SiO₂. As the island protrudes upwards, the lateral adatom adsorption also takes place at the island sidewalls, resulting in an increase of mean diameter of the island. This is consistent with the increase of mean feret diameter in 5nm case relative to the nanodisk [Fig.

5.5(b)]. In 10nm case, the process is dominated by facet formation, resulting in ever decreasing interfacial area which finally topples down the SiO₂ nanodisk. During the facet formation, the island base shape evolves from circular to quadrilateral so as to simultaneously increase the variation of feret diameter (σ_d) and decrease the mean diameter (μ_d), leading to an increase of δ [Fig. 5.5(c)]. However, it might be worth noting that due to transitory nature of the growth at this stage, the boundary lines between the 10nm-islands and the substrate are not clear, which may lead to errors in feret diameter measurement, because it is difficult to determine image thresholding.

Finally, in 20nm case, the catalytic growth is no longer present since the nanodisk toppling down is already apparent in 10nm case. Thus, the island growth is dominated by lateral adatom adsorption together with facet formation, resulting in more defined facets, which is clearly apparent in edge effect in SEM image, as shown in [Fig. 5.2(c)]. It is also expected that the feret diameter increases due to lateral adatom adsorption, which is consistent with the fact of increasing mean feret diameter and decreasing δ in Fig. 5.5(d). Overall, regardless of the nominal deposition thickness, the uniformity values of the islands are still not too far off from the uniformity of the SiO₂ nanodisks, showing the uniformity preservation we can achieve from this growth mechanism.

The errorbar plot (with max, min, and mean) of the lateral size distribution is shown in Fig. 5.6. It can be seen that the lateral size margin of the grown islands follows that of the SiO₂ nanodisk, irrespective of different nominal deposition thicknesses.

Figure 5.6. Errorbar plot of lateral size of the nanodisks and the islands.

Therefore, by controlling the diameter of the nanodisks, it is possible to have a control over the lateral size of islands. One may even think of the possibility to grow islands with the size approaching quantum dots by tuning the nanodisk size to close to sub-10nm.

We will now look into the height of the islands. The height of 5, 10, and 20nm islands is measured using Atomic Force Microscope (AFM) and the result is tabulated in Table 5.2 and Fig. 5.7.

	5nm-islands	10nm-islands	20nm-islands
σ_h (nm)	56.24	43.65	65.16
μ_h (nm)	5.01	7.33	10.34
δ_h (%)	8.91	16.79	15.87
counts	525	506	525

Table 5.2. Statistical data of height of 5nm-islands, 10nm-islands, and 20nm-islands.

Figure 5.7. Height histogram and representative three-dimensional view of the islands as obtained from AFM measurements of: (a) 5nm-islands; (b) 10nm-islands; (c) 20nm-islands.

It is interesting to note that for 5nm deposition thickness, the mean island height is 56.2nm, which is about 10 times the nominal deposition thickness. This shows that the adatom flux from outside of nanodisks is concentrated into the nanodisks area. From 5nm to 10-nm islands, the mean height reduces to 43.6nm. This again can be understood by considering that at this stage the islands are undergoing the transition

from disk-shaped to pyramidal shape. At 20nm-islands, the mean island height increases again to 65.2nm, which is consistent with the fact that the pyramid facets have become more defined.

5.6 Growth Model

The growth mechanism can be phenomenologically described as follows. Assuming the nanodisk array is perfectly periodic and there is no island growth outside the nanodisks, we can model the adatoms falling within a certain unit cell area as being concentrated in the nanodisk area due to the catalytic nature of the nanodisk. In the initial stage of the growth (i.e. $t = 0$), catalytic growth underneath the nanodisk mask can be described by $G_m A_0 = G_{nom} A_{cell}$, where G_m is the growth rate on the nanodisk mask, A_0 is the nanodisk area, G_{nom} is the nominal growth rate, and A_{cell} is the unit cell area. Thus, the initial catalytic growth rate is $G_m = G_0 (A_{cell} / A_0) = G_0 / f$, where $f = A_0 / A_{cell}$ is the filling factor. Thus decreasing the disk diameter while keeping the periodicity fixed will increase the initial growth rate by the same factor. However, when both disk diameter and periodicity are changed such that the filling factor is fixed, the initial growth rate is expected to remain constant.

When the mask starts to be lifted up by the growing island, lateral adsorption starts to take place on the island sidewalls, contributing to the island growth. The growth mechanism for islands grown on GaAs (100) substrate then can be described phenomenologically as

$$dV/dt = G_{nom} A_{cell} = G_m(f, t) A_{int}(t) + G_{LA} A_L(A_{int}, A_0, h, t) \quad (5.2)$$

where V is the volume of the island, A_{int} is the interfacial area between SiO_2 and GaAs, G_{LA} is lateral adatom adsorption rate, A_L is the total area of the island sidewalls on which lateral adsorption takes place, and h is the island height. The competition between catalytic growth, lateral adsorption, and facet formation can be represented by the above model, where the facet formation is implied in $A_{int}(t)$. It is important to note that this competition only occurs for (100) plane, where the catalytic growth is not self-sustaining due to preferential facet formation. This is to be contrasted when the growth is done in (111) plane, as with the case of VLS growth of III-V nanowires [2,3].

5.7 Investigation to the Nature of the Catalytic Agent

There are a few plausible reasons to regard the growth mechanism as catalytic:

1. The island pushes up the nanodisk, similar to Au particle catalyst being pushed up in VLS nanowire growth;
2. The flat-top island shape (plateau) in 5nm nominal deposition thickness case is a signature of the growth originated from interface between SiO_2 nanodisk and GaAs substrate;
3. The lateral size of the islands which closely corresponds to that of the nanodisks;
4. The uniformity of the islands follows that of the nanodisks.

Since GaAs islands are directly interfaced with SiO_2 nanodisks, it is reasonable to suspect that the SiO_2 material plays a role in the catalytic growth. Park et al. [5] has used highly reactive nanometer-sized Si clusters resulting from phase separation of SiO_x as a catalyst for InAs nanowire growth. We have done FTIR measurement on

the SiO₂ nanodisks on GaAs substrate to check the stoichiometricity of the SiO₂ nanodisks.

Figure 5.8. FTIR spectra of SiO_x nanodisks on GaAs substrate.

From the FTIR spectra we obtain the TO stretching peak of Si-O-Si bond to be located at 1062 cm⁻¹. This peak location obeys a linear relationship [6, 7]:

$$\nu(\text{SiO}_x) = 900 + 90x \text{ (cm}^{-1}\text{)} \quad (5.3)$$

where x is the oxygen content of SiO _{x} . If we input ν value as 1062, we will obtain x as 1.8. This shows that the nanodisks are non-stoichiometric with composition of SiO_{1.8}.

Zhang et al. [8] did quantum mechanical calculations to reveal that remarkably high reactivity at the Si atoms exists in silicon suboxide Si _{n} O _{m} clusters with $2n > m$. Therefore we hypothesized that it is likely that the reactive Si atoms, or Si nanocrystal, played the role as the catalyst in our growth. This is consistent with Ref. 5 where silicon nanocrystal acts as catalyst in that it acts as an opening for the incoming adatoms. To fully understand the catalytic mechanism, further investigations are needed in the future.

5.8 Potential Applications

5.8.1 As an alternative approach to grow uniform quantum dots

We believe that this growth mechanism has a potential to be an alternative patterned substrate approach, especially if the same mechanism can be demonstrated in heteroepitaxial quantum dot system. First, the catalysts guarantee the pattern transfer fidelity, i.e. the arrangement and size of the islands would closely follow those of the nanodisks. This is useful in applications of quantum dot as single photon emitter. Second, the combination of facet formation mechanism and unconstrained adatom movements is crucial in preserving the uniformity of the resulting islands. In conventional patterned substrate approach, the adatom movement is constrained within the holes or openings in order to grow the island [1, 9-13], and any non-uniformity of the holes (either on the base or on the sidewalls) would translate to non-uniformity of the islands. This is in contrast to our case, where the adatoms freely move around the nanodisks and are not limited by sidewalls, giving the island formation less hindrance to develop most energetically stable facets. Since facet formation is a natural phenomenon, when the facets have been well defined, the resulting islands would be uniform. In other words, facet formation mechanism is utilized as a “correction factor” to island uniformity. It is desired that in this approach, the uniformity of the islands would be less dependant on the uniformity of the patterns. We have seen earlier that the δ values of the SiO₂ nanodisks and of 20nm-islands are quite close (5.74% and 8.74%, respectively), showing that the uniformity of the original pattern is preserved.

The combination of the catalytic growth and facet formation renders this growth mechanism to be a directed self-assembly approach, where the term “self-assembly” here refers to the natural facet formation mechanism which is assisted by the greater freedom in adatom movement, and the term “directed” refers to the “catalyst” which determines the growth location.

5.8.2 Shape tunability

We also notice that the shape evolution is induced by different strength of the catalytic effect and facet formation at various stages of island growth, as described in the schematic and SEM picture of the islands in Fig. 3.8. When the nominal deposition thickness is 1nm, catalytic growth dominates, resulting in thin disk island shape. Increasing nominal deposition thickness results in facet formation working together with catalytic growth, resulting in unique island shape such as the 5nm-islands which has the slanted sidewalls from facet formation mechanism and flat top from catalytic growth. As we go further to 10nm and 20nm, catalytic growth is weaker than facet formation, and facet formation shapes the island into pyramidal shape. Therefore by controlling the strength of both mechanisms, it is possible to achieve various island shapes. The island shape evolution from disk-shaped to flat-top pyramid, and to faceted pyramid, shows that there is a potential to use the growth mechanism to tune of the shape of islands, i.e. island shape tunability.

Figure 5.9. Illustration of the competition between catalytic growth and facet formation in increasing nominal deposition thickness: (a) 1nm; (b) 5nm; (c) 10nm.

Further island shape tuning can be achieved by annealing, as shown in the result in Fig. 5.10. The nominal deposition thickness is 10nm, and the sample is annealed in-situ for 20 minutes in the growth temperature (630°C).

If we look at the as-grown results [Fig. 5.10(a)], it again seemed as if no growth had happened in the sample. After the nanodisk removal by HF, we find flat islands instead of pyramidal islands like before. The islands lateral size is about the same as the nanodisk size, which causes the islands to be “hidden” underneath the SiO₂ nanodisks. Another clue is obtained from the black holes surrounding the islands. These holes are also seen on the top view SEM picture of the as-grown islands,

underneath the transparent SiO₂ nanodisks. Therefore it appears that we could use annealing to further tune the island shape. The annealing gives energy for the adatoms to organize itself, subject to the influence of the SiO₂ nanodisks.

Figure 5.10. SEM pictures of samples deposited with 10nm nominal deposition thickness and annealed in-situ for 20 minutes: (a) as-grown; (b) after removal of silica nanodisk.

Another interesting result comes from nominal deposition thickness of 50nm, as shown in Fig. 5.11. The islands seem similar to 20nm-islands, i.e. the facets are fully defined. However at many other areas there is overgrowth outside the nanodisks. This proves the concept of equilibrium crystal shape which states that when pyramidal islands have formed the most stable facets, the islands would stop growing despite the continuing influx of new material.

Figure 5.11. SEM images of the sample deposited with 50nm nominal thickness, after mask removal: (a) areas where islands are orderly arranged, the inset shows enlarged view of one island; (b) areas where overgrowth around the islands are seen.

As a summarized discussion, the strategy to control shape, size and size distribution of the islands is to use the combination or the interplay of catalytic growth and facet formation. While facet formation is an internal force by virtue of the crystal structure of the substrate and the islands, catalytic growth may be controlled externally by controlling the strength of the catalyst (in terms of resulting growth rate) e.g. by tuning different composition of SiO_x .

5.9 Summary

In this chapter we have reported the growth results from silica nanodisks-patterned GaAs (100) substrate. The islands grew from underneath of the silica nanodisks to form a pyramid, and at some point topple off the silica nanodisk. The islands follow the size and the arrangement of the silica nanodisks closely. The growth mechanism

is attributed to catalytic growth, facet formation, and lateral adatom adsorption. We have also discussed the potential applications of this growth mechanism as an alternative patterned substrate approach to grow quantum dot; and as a method to achieve size and shape-tunable islands/dots.

Chapter 6: Conclusion and Future Works

6.1. Conclusion

In this thesis, an alternative method of island growth which combines external patterning and internal forces have been explored and demonstrated. The work can be divided into two main stages: (1) the template patterning, and (2) the island growth. In the template patterning stages, various methods have been explored for realizing silica nanodisks with differing shapes, sizes, and arrangements. The first two patterning methods are based on self-assembly of polystyrene (PS) nanospheres. The first method is based on spin coating PS nanospheres on a substrate where a quasi monolayer of PS nanospheres was realized. The pattern was then transferred into silica by means of dry etch. The drawback of this method is that the hexagonally closed packed silica nanodisks were formed together with triangular openings which arose from bilayered PS nanospheres. The second method is based on a modified nanosphere lithography which utilized surface tension and surfactant in forming a large area of monolayered PS nanospheres. The area within which the PS nanospheres array is monolayer spans over few cm^2 areas, which is good for our growth purposes.

The last two patterning methods are based on electron beam lithography (EBL). The third patterning method is based on negative tone HSQ resist whereby amorphous silica (SiO_x) patterns are formed out of e-beam exposure. Thus far, SiO_x pattern with sizes down to 20nm with height of 42nm have been successfully demonstrated. Such dimensions are approaching the dimension of quantum dots themselves, which is in order of sub-20nm. The presence of adhesion problem in HSQ based pattern can be

minimized by depositing a thin layer of SiO₂ beneath HSQ layer. The fourth patterning method is based on positive tone ZEP resist whereby Ti-Au was evaporated into sub-50nm openings defined by EBL. In order to ensure the evaporated metals to go through the narrow openings, it is instructive to increase the dose. Thus far, metal patterns with sizes down to 23nm have been demonstrated. Therefore, in this work, the lift-off technique has been optimized to realize sub-50nm metal pattern of 20nm height.

Despite being low in throughput, it should be noted that the generated HSQ and ZEP patterns possess a high degree of information in terms of sizes, shapes, and geometrical arrangement. In addition, the pattern can be uniquely defined and positioned as desired according to the designer's point of view. This is in contrast with the first two methods, where achieving a monolayer (or hexagonally close packed structures) of PS nanospheres becomes a necessity before size tunability can be implemented (by means of dry etch, for example). Thus, although high throughput in nature, the patterns exhibit little amount of information since the structure will always be ordered and have uniform size and shapes.

In the island growth stage, GaAs islands have been successfully grown on GaAs(100) substrate by Solid Source Molecular Beam Epitaxy (SS-MBE) based on the nanosphere lithography patterning. The growth mechanism is believed to be based on catalytic growth and facet formation. The uniform and ordered island formation over a large area (~50μm x 50μm) suggests the feasibility of the mechanism to overcome the stringent requirement over mask uniformity in conventional patterned substrate approach. It is believed that the presence of silicon

nanocrystal acts as catalyst in that it acts as an opening for the incoming adatoms. This is in consistency with FTIR measurement which indicated non-stoichiometricity of SiO_x film, where x was found to be 1.8. Further investigation is still needed with regards to the nature and the mechanism of the catalyst.

The statistical distribution of island lateral size shows that the lateral size and the uniformity of the islands follows the lateral size and the uniformity of the SiO_x nanodisks closely, e.g. the uniformity value of the nanodisks is 5.74% whereas the uniformity value of the 20nm-nominal-deposited-islands is 8.74%. This shows the pattern transfer fidelity we can achieve from this growth mechanism.

6.2. Future Works

Thus far, the catalytic island growth was demonstrated in the pattern generated by the nanosphere lithography. However, the catalytic island growth has not been demonstrated in the EBL based patterns. The ultimate goal of nanotechnology would be to manipulate objects in nanometer size, including the size and shape tunability in three dimensional sense. First, if the cause of catalytic growth is indeed the presence of silicon nanocrystal in SiO_x film, we believe that the HSQ-based patterns would have a great potential to realize variable shape island growth. In addition, by annealing exposed HSQ in hydrogen environment it is possible to tune the nonstoichiometricity of the SiO_x material, which could possibly control the strength of the catalytic effect. Second, the gold induced catalytic growth thus far has been demonstrated mainly in the growth of III-V semiconductor nanowires. We believe that the island growth based on metals would be a contribution in catalytic growth

research. Finally, if the patterns can be as small as 20nm (or even less, depending on EBL process optimization), then the next logical step would be to realize the catalytic heteroepitaxial growth of III-V quantum dots. If the above future works are demonstrated, we believe this would be a step closer towards the vision of nanotechnology.

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Chapter 2

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List of Publications

1. Liliana Tjahjana, Benzong Wang, Hendrix Tanoto, Soo-Jin Chua, and Soon Fatt Yoon. "Gallium arsenide (GaAs) island growth under SiO₂ nanodisks patterned on GaAs substrates". *Nanotechnology*, 21 (2010) 195305.
2. L. Tjahjana, L. Y. M. Tobing, B. Wang, H. Tanoto, S.J. Chua. "Disk-to-Pyramidal GaAs Islands Shape Evolution on Nanodisks-Patterned Substrate". *Proceeding of IPGC 2008 (IEEE Photonics Global Conference)*, 8-11 December 2008, Singapore. Oral presentation, A3-2A-03. Indexed in IEEE Explore: Digital Object Identifier: 10.1109/IPGC.2008.4781328.

Conference Presentations

1. Tjahjana, Liliana; Tobing, Landobasa; Wang, Benzong; Yoon, Soon Fatt; Chua, Soo Jin. "An Unusual Island Formation Phenomenon on Disk-Patterned Substrate". *ICMBE 2008 (International Conference on Molecular Beam Epitaxy)*, 3-8 August 2008, Vancouver, Canada. Oral presentation, TUB2.3.
2. L. Tjahjana, L. Y. M. Tobing, B. Wang, H. Tanoto, S.J. Chua. "Disk-to-Pyramidal GaAs Islands Shape Evolution on Nanodisks-Patterned Substrate". *IEEE Photonics Global Conference*, 8-11 December 2008, Singapore. Oral presentation, A3-2A-03. Indexed in IEEE Explore: Digital Object Identifier: 10.1109/IPGC.2008.4781328.