

GROWTH AND CHARACTERIZATION OF III-V COMPOUND
SEMICONDUCTOR NANOSTRUCTURES BY METALORGANIC
CHEMICAL VAPOR DEPOSITION

BY

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THESIS

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ABSTRACT

Planar $\langle 110 \rangle$ GaAs nanowires and quantum dots grown by atmospheric MOCVD have been introduced to non-standard growth conditions such as incorporating Zn and growing them on free-standing suspended films and on 10° off-cut substrates. Zn doped nanowires exhibited periodic notching along the axis of the wire that is dependent on Zn/Ga gas phase molar ratios. Planar nanowires grown on suspended thin films give insight into the mobility of the seed particle and change in growth direction. Nanowires that were grown on the off-cut sample exhibit anti-parallel growth direction changes. Quantum dots are grown on suspended thin films and show preferential growth at certain temperatures. Envisioned nanowire applications include twin-plane superlattices, axial pn-junctions, nanowire lasers, and the modulation of nanowire growth direction against an impeding barrier and varying substrate conditions.

To my mother, father, and sister

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1. INTRODUCTION

1.1 Compound Semiconductors

Compound semiconductors are a very versatile class of semiconductors. Typically formed from periodic elements from groups III and V, or II and VI, they provide material properties that are useful for a number of electrical and optical devices. They provide such advantages as a direct bandgap, enhanced carrier mobility and the creation of ternary and quaternary materials that have fine-tunable electronic and optical properties based on material composition. This also allows the creation of functionalized layers that can be utilized in other ways, such as utilizing specialized growth phenomena, sacrificial layers and strained layers which are of use to create novel nanostructures such as semiconductor nanotubes [1], III-V semiconductor nanowires [2], and self assembled III-V quantum dots [3]. This research focuses mainly on nanostructures consisting of III-V semiconductor materials.

1.2 Crystal Structure

III-V materials are comprised of at least two different atoms that sit on a crystal lattice. III-V crystal structures can occupy different crystal structures, two of the most common polytypes being wurtzite and zinc-blende. Wurtzite is a hexagonal crystal structure with alternating atoms (unlike simple hexagonal close-packed, which has alternating uni-atomic layers) that follow an ABAB alternating layer structure, while the zinc-blende structure resembles a normal cubic lattice but with a diatomic basis resulting in a structure that resembles two BCC crystals interlaced with each other with an ABCABC layer structure. Since both zinc-blende and wurtzite crystal structures of III-V materials have a diatomic basis, resulting in

alternating layers of material, they are prone to crystal defects. One of the main defect types is the stacking fault. For example, in wurtzite a stacking fault would be ABABBA, where the two B layers sit on top of each other instead of alternating between A and B. A special type of stacking default that can occur in zinc-blende crystals (but not in wurtzite due to its mere 2 layers) is a twin defect, in which the crystal layers reverse order after a stacking fault. For example, a twin defect would be ABCABCBCBA, where the original crystal order was ABC but shifted to CBA. Polytypism is another type of growth phenomena where the crystal structure changes, such as shifting from zinc-blende to wurtzite.

In the case of crystal growth, growth of polar semiconductor materials on single crystal elemental semiconductor substrates can be problematic. Polar crystals, crystals with a diatomic basis that results in differently charged atoms, behave differently than elemental crystals (such as Si and Ge). Polar crystal grown on elemental crystal are usually wrought with defects called anti-phase domains. Anti-phase domains occur when there is a monoatomic step on the surface of the substrate and the deposited crystal is of a different crystal structure (i.e., zinc-blende structure on a Si substrate) [4]. The step causes two like atoms to bond together, instead of two dissimilar atoms. For example, normally GaAs bonds with Ga-As atoms, where an anti-phase domain would bond Ga-Ga due to a monoatomic step on the Si substrate, hence causing a defect.

When growing heteroepitaxial crystals, the effects of strain should be considered. The atoms in a crystal like to situate themselves at specific distances from one another. This bond length dictates the length of the unit cell, the repeated atomic structure throughout a crystal, which is also referred to as the lattice constant. In heteroepitaxy, when materials are deposited on a substrate with a different lattice constant, there is a strain that is induced. If the material grown has a larger lattice constant, the grown crystal is compacted and a compressive strain is created.

Suppose the crystal grown has a smaller lattice constant; then the atoms are pulled apart to accommodate the substrate, forming a tensile strain. If the strain is too high, the bonds will break and dislocations will form a metamorphic layer. Induced strain can also influence the bandgap of crystals by adjusting the interatomic spacing. Compressive strain will cause the bandgap to widen, as well as lifting the heavy hole band above the light hole band in the valence band. Tensile strain shrinks the bandgap with the light hole band, raising it above the heavy hole band. Strain can also influence the effective mass by altering the curvature of the band edges. Crystal defects and strain are major concerns for III-V crystal growth on elemental crystal substrates. The polyatomic nature of compound materials gives rise to issues that affect both crystal growth as well as electronic and optical properties which will be further expounded upon.

1.3 Electrical Properties

In relation to semiconductor physics, some III-V semiconductors have phenomena occurring that are not present in elemental semiconductors. Using GaAs, for example, phonons are a contributing source of carrier scattering. When phonons, acoustic or optical, propagate through the crystal lattice, they distort the lattice and create a deformation potential by locally changing the band structure through changing the inter-atomic spacing of the crystal. In polar crystals, the lattice can also be distorted by a charged carrier moving through the crystal distorting a lattice; this is called a polaron. Due to the symmetrical nature and high curvature (low electron effective mass) of the GaAs conduction band minimum, electrons are unaffected by optical deformation potential scattering and resistant to acoustic phonon scattering. This leads to a high electron mobility which can be utilized to create high speed devices that are difficult to realize in elemental semiconductors. Unfortunately, the high electron mobility usually leads to a

disparity between electron and hole mobility, which is generally considered detrimental for CMOS technologies. Improving hole mobility has been an active area of research in the field of III-V electronic devices [5].

1.4 Optical Properties

III-V semiconductors have an important optical feature that distinguishes them from elemental semiconductors: the direct band gap. In elemental semiconductor, Si or Ge, the conduction band minima and valence band maxima do not share the same point in k-space. This means that for an electron in the conduction band to radiatively recombine with a hole in the valence band, it needs a shift in momentum to allow this to occur. Usually the source of momentum change is a phonon to assist it, so radiative recombination in indirect materials is limited by the availability of suitable phonons for light emission. This holds true for absorption processes. Much of light conversion efficiency is lost in indirect materials due to non-radiative recombination such as the Auger effect or phonon emission [6]. With direct bandgap semiconductors, there is no intermediate step and they have much higher light conversion efficiencies, making them choice materials for optical devices. Also, utilizing ternary and quaternary compounds allows engineers to adjust the bandgap of materials to alter their absorption/emission spectra according to the application of the device. Polar crystals also exhibit special types of optical phonons, where two atoms vibrate against each other at high frequency due to coulombic effects between the crystals, called polar optical phonons. These phonons couple readily with light, producing a new quasi particle—the polariton—which has been investigated by researchers for new potentials in optical devices [7].

Nanostructures allow engineers to control the possible energy states available within a semiconductor device through dimension-induced band structure change. While electrons appear to have a quasi-continuum of available states within bulk materials, electronic states can be further quantized by controlling the size of the nanostructure. As the dimension of a nanostructure approaches the order of magnitude of the de Broglie wavelength of the carriers, the states start to spread out and become quantized. Figure 1.1 graphically shows the relationship between density of states and energy for different degrees of confinement. If one direction of a nanostructure is confined (i.e., quantum wells), the density of states is constant for each sub-band [4]:

$$g(E)^{2D} = \frac{L^2 m^*}{\pi \hbar^2} E$$

where L is the unconfined length, m^* is the effective mass, E is energy and \hbar is the reduced Planck's constant. If two directions are confined (i.e., quantum wires), the density of states sharpens and follows the following equation, the 1D density of states (for one sub-band) [4]:

$$g(E)^{1D} = \frac{2L}{\pi} \left(\frac{2m^*}{\hbar^2} \right)^{\frac{1}{2}} E^{-\frac{1}{2}}$$

If all three dimensions are confined (i.e., quantum dots), the DOS is simply a delta function. This is useful for optical devices where one can tune and narrow the emission spectrum by controlling the degree of confinement, which is important for specific wavelength devices such as lasers and LEDs.

While III-V nanostructures are a heavily researched field, there is still much to learn and improve upon. Dopant and isoelectronic impurity incorporation in III-V VLS nanowires is still under heavy investigation. Researchers are still unsure about whether the impurities diffuse through the nanowires or into the colloid itself. Planar nanowires have a distinct feature in which they interact heavily with the substrate along their entire length. Placing them in scenarios with alternating substrates may prove beneficial to understanding their intricate nature. The growth of III-V on silicon has been an age-old problem for crystal growers. Growth on suspended silicon membranes may play an important role in solving this dilemma, as well aid in the process of ordering quantum dots without the need for lithography. This work intends to tackle and shed light on these topics.

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1.6 Figures

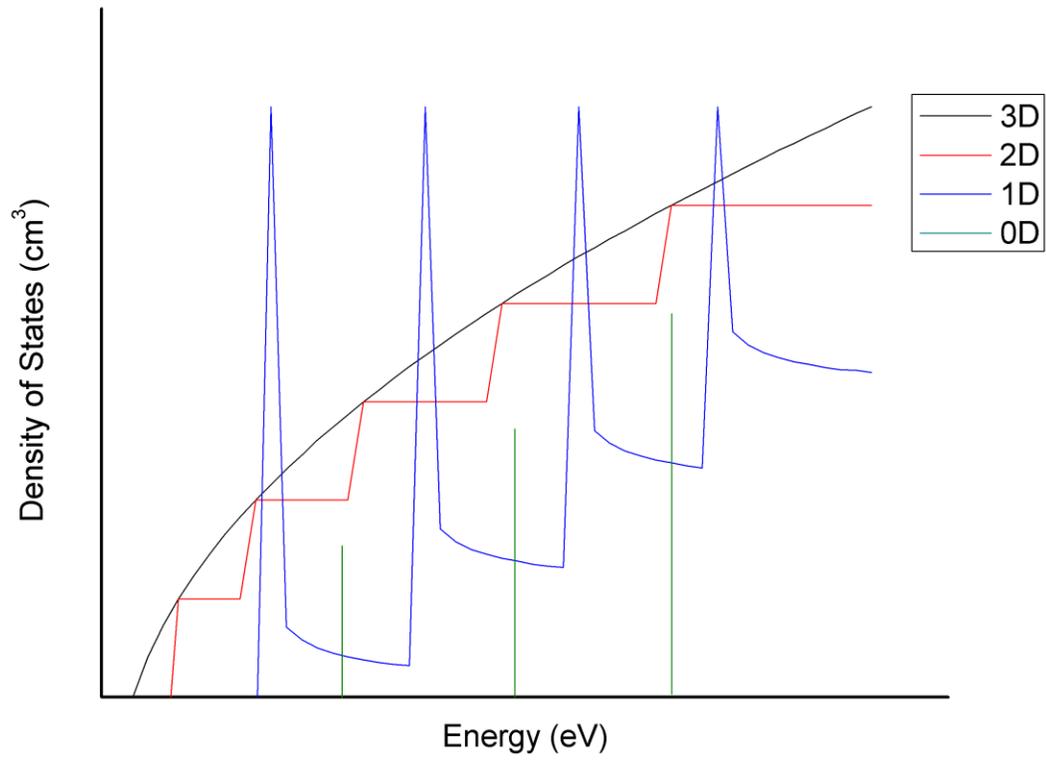


Figure 1.1 Graph showing the relationship between density of states and energy for various dimensions of confinement.

2. EXPERIMENTAL DETAILS

2.1 Metalorganic Chemical Vapor Deposition

Metalorganic chemical vapor deposition (MOCVD) is a specialized form of CVD that is used to deposit epitaxial films. Typically MOCVD is used to deposit compound semiconductors, but it can also be used to deposit elemental semiconductors such as silicon and germanium. Compound semiconductors grown by MOCVD offer a wide variety of benefits such as adjustable material composition, in situ doping of grown layers and faster growth rates than other deposition techniques like molecular beam epitaxy (MBE). Film deposition is produced by flowing in a metalorganic precursor such as trimethylgallium (TMGa) for gallium, or trimethylindium (TMI) for indium, and a hydride such as arsine (AsH_3) for arsenic or phosphine (PH_3) for phosphorous, into a reactor chamber. High purity hydrogen (H_2) and sometimes nitrogen (N_2) gas are commonly used as carrier gas. The precursor molecules pyrolyse, or crack, under high temperature and deposit the desired material on the surface of the sample while the gaseous byproduct and unreacted precursors are swept to the exhaust. Dopant precursors can be flown during crystal growth to form doped epitaxial films. Dopants can either be incorporated through a metalorganic source, such as dimethyl zinc (DMZn) or a hydride source such as silane (SiH_4) or disilane (Si_2H_6). An interesting phenomenon occurs in III-V materials when doping is considered. Since they contain atoms from both group III and group V, their dopants can behave amphoterically. This means that the dopants can either behave as n-type dopants or p-type dopants depending on which lattice site they sit on. Usually the dopant type, growth temperature and other growth conditions dictate how the dopant behaves.

In thin film epitaxy there are three growth modes that govern crystal epitaxy depending on growth conditions [1]. The first growth mode occurs when films are relatively lattice-matched and are comparable. As adatoms attach to the surface they form a very thin wetting layer. This thin layer forms evenly on the surface, forming a high quality thin epitaxial film. This growth mode is called layer-by-layer growth, or Frank van der Merwe growth mode. The second growth mode, Volmer-Weber growth, is the formation of large islands of crystal, usually metamorphic. This growth mode is achieved either when adatoms prefer to aggregate with each other instead of attaching to the substrate, or when strain interaction is too high with the substrate and formation with other adatoms is preferential. This resulting growth is usually entirely 3D, riddled with dislocations and defects at the growth interface. Lastly, the third growth mode is a combination of the first two, when the thin wetting layer forms but adatoms merge to form a 3D growth on top of an often pseudomorphic 2D wetting layer. This growth mode, Stranski-Krastinov, is highly desirable in the formation of nanostructures, especially quantum dots. This allows for the benefit of a 3D structure with the high quality interface of a 2D epitaxial film.

2.2 Vapor-Liquid-Solid Growth

In 1964, Wagner and Ellis [2] discovered a method to create such 1D structures via CVD growth. These whiskers (now commonly referred to as nanowires) were fabricated by a mechanism called vapor-liquid-solid growth. Metal is deposited onto the surface of a single crystalline semiconductor by evaporation, sputtering or in colloid form. A liquid metal particle forms between the metal and the semiconductor when the substrate is heated above the eutectic temperature of the alloy. A vapor phase precursor is introduced into the reactor, decomposes on the surface of the particle, and diffuses inward. Once the particle becomes super-saturated and a

single-crystalline solid is precipitated out the particle. This results in an extremely anisotropic nanowire with well-defined crystal facets and a diameter that is dependent on the size of the particle.

Usually, nanowires are grown in non-planar directions with the $\langle 111 \rangle$ direction being one of the most common. The issue with non-planar wires is that they are hard to integrate with traditional planar devices (CMOS, optoelectronics) without removing them from their host substrate. Interestingly enough, under the right growth conditions, planar nanowires can be grown epitaxially on the surface; $\langle 110 \rangle$ GaAs nanowires can be grown planar on $\langle 100 \rangle$ GaAs substrates. While nanowires have been researched extensively for the last decade, planar GaAs nanowires still have to be fully characterized since the controlled growth of planar nanowires was first reported by our research group in 2008 [3]. This work discusses some of the efforts to characterize the effect of Zn doping, In incorporation, suspended thin membranes and off-cut substrate growth of $\langle 110 \rangle$ planar GaAs nanowires.

Planar $\langle 110 \rangle$ GaAs nanowires are grown by in a Thomas Swan atmospheric MOCVD reactor. The MOCVD reactor is a vertical setup utilizing a quartz chamber, with a graphite susceptor that is heated via an RF generator and growth substrates are (100) semi-insulating GaAs. Trimethylgallium (TMGa) and trimethylindium (TMI) are used as the group III sources while AsH₃ is used as the group V hydride and diethylzinc (DEZn) is utilized as the Zn source. H₂ is used as the carrier gas. Au colloid, with sizes ranging from 20 to 250 nm, suspended in an aqueous solution is deposited on epi-ready (100) semi-insulating GaAs wafers. Excess water is removed through evaporation by simply heating the sample on a 115 C° hotplate. To create suspended films, 50 nm of GaAs are grown on top of 1 μm of Al_{0.75}Ga_{0.25}As on GaAs substrate. Bowtie shaped patterns are used to create an area of suspended and supported GaAs for nanowire

synthesis to occur. The lithography pattern is transferred to the GaAs by a 1:8:80 H₂SO₄:H₂O₂:H₂O etch, and then the sacrificial Al_{0.75}Ga_{0.25}As layer is removed by a 49% HF etch. For the suspended structures, Au is deposited prior to lithography and wet chemical etching for two reasons: (1) to prevent stiction [4] and damage to the suspended film due to the drying action of the Au colloid solution and (2) to reduce variability of Au colloid density across the sample by having some colloid naturally rinsed away during processing.

Before metalorganics are flowed, the samples are heated to 625 C° in situ for 10 min in the presence of AsH₃ (to prevent arsenic desorption from the substrate) in order to remove the native oxide and anneal the gold colloid before growth. With the suspended film, wires are grown at 460 °C with a targeted growth rate of 43 nm/s. The control flow rates are 10 sccm of TMGa with AsH₃ ranging from 200 sccm during the oxide desorption step and increased to 500 sccm during the actual growth. For the impurity effect tests, molar flow ratios of impurity to TMGa range from 8.0×10^{-5} to 2.0×10^{-2} . The wires are first grown halfway for 70 s with just TMGa and AsH₃ present, then after a 15 s pause the impurities are flown with TMGa for another 70 s. After growth, the samples are cooled in the presence of AsH₃ for 5 min. Nanowires were characterized post growth by a Hitachi S4800 scanning electron microscope (SEM) and 15 kV at also with a JEOL 2010 LaB₆ transmission electron microscope (TEM).

2.3 Preparation of Silicon Membranes and Quantum Dot Growth.

The growth of III-V self-assembled quantum dots on thin silicon suspended membranes is a two-step process. The substrate is a silicon-on-insulator wafer supplied by Soitec and provided to us by Max Lagally's group at the University of Wisconsin at Madison. The manufacturing process of SOI wafers can be viewed at the Soitec web site [5]. For our

experiments, the thickness of the silicon active layer is 25 nm or 13 nm. A pattern of various squares sized $20 \times 20 \mu\text{m}^2$, $10 \times 10 \mu\text{m}^2$, $5 \times 5 \mu\text{m}^2$ and $2 \times 2 \mu\text{m}^2$ are formed via photolithography followed by reactive ion etching. Photoresist is then stripped and thoroughly cleaned by degreasing using a combination of acetone, methanol and isopropyl alcohol to remove any organic materials. The suspended edge is created by using the buried oxide as a sacrificial layer to undercut the silicon on top of the insulator. A dilute 1:10 HF:H₂O is used for 15 min in order to create a proper undercut. The undercut is around 1 μm from each edge of the square pattern, with the $2 \times 2 \mu\text{m}^2$ squares being removed as an indicator of proper etching. The samples are dried then loaded into the MOCVD reactor chamber to begin growth.

The Thomas Swan atmospheric MOCVD reactor is used for quantum dot growth as well. The samples are prepared the same way as nanowire samples except that AsH₃ is not flown during the desorption step as there is no concern for arsenic desorption for a silicon substrate. TMGa is used as the gallium precursor and AsH₃ as the hydride source. The nominal growth temperature is 450 C° during the deposition of the quantum dots and is maintained during the growth interruption. The nominal time for the growth interruption is 30 s; during this time AsH₃ is switched off with only carrier gas flowing to prevent hydrogen incorporation into the quantum dots [6], and to allow their proper formation. After the growth interruption, AsH₃ is switched back on and the temperature is cooled down to ambient. The dots are then characterized by SEM in a Hitachi S4800 scanning electron microscope. Correlations between growth conditions and quantum dot results are discussed further in the quantum dot chapter in this work.

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3. VAPOR-LIQUID-SOLID NANOWIRES

3.1 Zinc Perturbation of Planar Nanowire Growth

Zinc is an important p-type dopant in gallium arsenide based III-V semiconductors. It is a non amphoteric dopant (unlike silicon), does not have the etching issue of carbon tetrabromide [1] and is readily available in its metalorganic form (DEZn or dimethylzinc (DMZn)). It does have its drawbacks as zinc is also known for being highly diffusive [2] in epitaxial GaAs films. In order to create electronic and photonic nanowire devices, understanding the mechanism behind how Zn is incorporated in VLS nanowires is essential. Zinc implantation [3] and in situ incorporation of zinc in vertical $\langle 111 \rangle$ nanowires [4] have been investigated. It has been confirmed recently that Zn incorporates through the metal catalyst in GaAs VLS nanowires [4]. It was also found that at certain precursor levels Zn encourages the formation of zinc-blende (in contrast to wurtzite) InP nanowires [5]. This phenomenon was used to create periodic twinning structures in nanowires at Zn incorporation levels above $1e18 \text{ cm}^{-3}$.

To illustrate the effect of Zn incorporation in our planar nanowire growth, a two-step growth scheme is used, starting with a Zn-free growth segment followed by turning on the DEZn source while keeping all other growth conditions constant. Figure 3.1 displays SEM images of Zn-doped GaAs growth effects as a function of Zn doping concentration. Clearly, without the presence of Zn, our planar nanowire growth condition favors the $\langle 110 \rangle$ orientation in the plane of (100), and extends the zinc-blende structure of the substrate epitaxially in the axial direction, as reported previously [6]. At Zn/Ga gas phase molar ratios above 0.8% ($3.6e19 \text{ cm}^{-3}$), nanowires immediately deviate from their planar growth trajectory and take off in directions that seem random but twist back and forth around $\langle 111 \rangle$ (Figure 3.1a). No wires remain planar as soon as

DEZn is switched on above this molar ratio. This implies that Zn incorporation at this level lowers the formation energy of non- $\langle 110 \rangle$ growth orientations, particularly the $\langle 111 \rangle$ solid-liquid interface, and thus steers the growth orientation off the $\langle 110 \rangle$ path. When the Zn/Ga ratio is lowered by an order of magnitude to 0.08% ($3.6 \times 10^{18} \text{ cm}^{-3}$), nanowire growth remains planar (Figure 3.1d) but exhibits characteristic “periodic notching” along the surface of the nanowire and side facets. We also have found that the period length between notches is on the same order of magnitude ($\sim 0.91 \times$) as the seed particle size, as shown in Figure 3.2, which suggests that the notching period is controllable depending on the seed particle size chosen. In addition to the notching, some solid precipitants have been observed on the surface of the Au colloid, as shown in Figure 3.3; these are more prevalent in the 0.08% Zn/Ga molar ratio, implying that the precipitates could be Zn rich.

To better understand the mechanism of the “notching” in the wire, TEM was performed. TEM samples were prepared by growing a 5 nm layer of GaAs on a sacrificial 1 μm layer of $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$. Etchant holes were created in the thin GaAs layer to allow HF better access to remove the sacrificial layer more readily. Once the nanowires were released, they were sonicated into methanol and then dispersed on a carbon TEM grid. Utilizing this method reduces the time and luck needed with other TEM preparation methods such as lift-out and thinning the sample until it is electron-transparent. The TEM image of the planar nanowire displayed in Figure 3.4 was taken by a JEOL 2010 LaB6 TEM. Twin planes are observed near the notches. Notably, twin planes are not perpendicular to the wire orientation, switching instead in the $\langle 111 \rangle$ crystal direction between the $\langle 111 \rangle_{\text{B}}$ and $\langle 111 \rangle_{\text{A}}$ crystal segments. In contrast, characteristic notches and ridges have been reported as twinning superlattices perpendicular to the wire growth direction in $\langle 111 \rangle$ InAs [7], GaP [8] and InP nanowires [5]. These groups have also reported

polytypic growth, controlling the formation of, and switching between, wurtzite and zinc-blende. While the twinning is highly periodic, the spacing between $\langle 111 \rangle_B$ and $\langle 111 \rangle_A$ crystal sections is uneven in the twinned planar nanowires. The $\langle 111 \rangle_A$ sections are approximately a quarter of the length of the $\langle 111 \rangle_B$ sections. Controllable periodic twinning shows promise for creating devices that require periodic differences in energy potentials, such as tunneling devices.

To examine the Zn doping profile along the planar GaAs nanowires growth direction, we resort to one-step growth where Zn precursor is turned on at the same time as the Ga precursor and remains at the same ratio throughout the nanowire growth. Shown in Figure 3.5 is the evolution of growth orientation and topography as Zn-doped GaAs nanowire growth proceeds for a gas phase DEZn/TMGa doping ratio of 0.08%. Interestingly, wires grown at this ratio that appear to be planar initially (as in Figure 3.1b) become non-planar after some critical distance, yet this did not occur with the 0.008% nanowires. This implies that zinc incorporation in nanowires increases over time until it reaches a critical point where it perturbs normal nanowire growth. Our observation is consistent with a previous report [4] on $\langle 111 \rangle$ vertical nanowires in which Zn doping increases gradually along the growth direction under constant Zn precursor flow. This may be attributed to the longer saturation time for Zn in Au compared to Ga in Au, leading to a delayed or accumulation effect of Zn impurity, which has been observed by Gutsche et al. [4] in their studies of p-type doping in vertical GaAs nanowires. This is an important property to take note of when considering what doping concentrations are appropriate for device dimensionality such as the channel length of a FET, as well as the possibility of creating a natural doping concentration gradient within the wire without extrinsically changing the flow rate for the creation of modulation doped nanowires.

It is remarkable that Zn incorporation at levels as low as 0.008% in planar GaAs nanowires is sufficient to alter the atomic structure (twin plane formation) and crystal orientation. This phenomenon presumably originates from the nucleation process in the VLS mechanism, where any perturbation at the atomic level, such as dopant incorporation, can be critical to the free energy of the interface between metal catalyst and solid surface, and the edges.

3.2 Suspended Film

To further explore the parameters that influence the VLS nanowire growth mechanism, we investigated growth on suspended thin film membranes. Membranes have been reported to have properties that are different for growth than normal bulk substrates. The main property that makes them so attractive is their ability to be more compliant [9] with nanostructures that cause stress because there is no restoring force on the backside of the suspended film. This allows suspended film to accommodate structures that were not realizable on bulk substrates. Another benefit of suspended films is the possibility of allowing epitaxial growth to occur on both sides of the film, enabling the prospect of double-density nanostructures.

Figure 3.6 shows the results that were observed in the SEM. First we observe a shift in growth direction not normally seen on bulk substrates. Normally planar nanowires grow in the $[0-11]$ and $[01-1]$ directions, but on suspended films wires have been observed growing in the $[011]$ and $[0-1-1]$ directions. This is indicative of how important the substrate conditions are for nanowire growth. Further modulation of nanowire growth directions may be possible by thinning the suspended film even more or changing other properties of the film. Next we noticed large holes were created in the suspended film, usually with a nanowire growing at the end of the hole that developed. We concluded that this was due to the Au particle alloying with the GaAs

suspended film during the anneal phase. It is interesting to note how much of the substrate the Au particle actually consumes during annealing and how mobile the gold is on such thin films. Another phenomenon of interest is that some nanowires actually grew off the edge of a suspended direction, grew normal to the substrate then collided with the surface and then grew in non-planar directions. This has been observed in Si nanowires with the use of oxide [10] as a sacrificial layer, but without a change in growth direction. These results hint at the future of creating 3D nanostructures by intentionally altering nanowire growth directions to fabricate elaborate nanowire arrays. Lastly, we have witnessed the guiding of nanowire growth by guiding it along a high step barrier. Figure 3.6c shows the nanowire periodically changing growth direction within the family of $\langle 110 \rangle$ direction as it grows along a barrier that is angled along a $\langle 100 \rangle$ direction. The barrier forms as a result of the undercutting of the GaAs suspended film; the nanowire is following along the $\text{Al}_{0.75}\text{GaAs}$ layer. The zigzag-like pattern is highly periodic and new physics could be unearthed in such an alternating pattern. Modulation of the nanowire growth direction increases the likelihood of nanowires being a fundamental building block for future nanotechnology devices.

3.3 Indium Perturbation

Indium is an important element in the synthesis of compound semiconductors for its capability of not only lowering the bandgap energy in ternary and quaternary materials but also functionalizing films by inducing strain from its larger atomic size. Incorporating indium into the core of GaAs wires will be essential in improving the variety of heterostructures that can be fabricated such as lasers, transistors [11] and diodes from nanowires. However, since indium notably changes the lattice structure, the possibility of indium incorporation perturbing growth

direction in planar nanowires was investigated in this report. TMI was turned on halfway into growth to see whether the presence of indium would alter the growth direction of the already planar nanowires and compare to the results of the Zn doping experiments. In/Ga molar ratios from 8.0×10^{-5} to 2×10^{-2} were investigated as well as two independent growths not included in the DOE with molar ratios that would be equivalent to an $\text{In}_{.50}\text{GaAs}$ and InAs film. Visual inspection shows that growth direction and crystallographic integrity remain intact although some nanowires exhibit a sharp notch approximately when TMI is turned on; however, this is not systematic across all wires and could be attributed to the 15 s pause time when no metalorganics are flown. This result is unexpected, especially since other groups have done work on fabricating InGaAs wires and observed changes with increasing TMI flow rates [12]. Interestingly enough, the growths with the higher indium contents produce reduced wire growth (dominantly in the $\langle 111 \rangle$ direction) and drastically increased epi-growth on the surface. Figure 3.7 shows that there is significant growth on the surface. This epi-growth resembles a metamorphic film that is discontinuous along the surface with large porous holes throughout. There are also no visible planar wires on the surface. Whether the change is caused by the surface impinging on planar growth, strain inducing overgrowth on the surface, or presence of indium in the core of the nanowire remains unknown without further analysis. Figure 3.8 shows that when nanowires are grown with conditions suitable to grow an InAs layer, virtually no nanowires are formed, and inspection reveals considerable growth on the surface. Furthermore, large trapezoidal shaped InAs mesas form on the surface that resemble the shape of gold bars.

The combination of DOE and the two independent growths leads us to two possible conclusions. First, inside the gold colloid there could be competition between In and Ga to form an alloy with Au. With the catalyst becoming supersaturated with gallium from the substrate

during the 10 min anneal step, perhaps the Au-Ga alloy inhibits indium inclusion and limits the amount of indium that will be incorporated into the wire and therefore leads to excess overgrowth on the surface of the substrate. Another possibility could be that indium prefers growth on the surface of the GaAs substrate over alloying with the gold catalyst. Dick et al.'s experiments with InAs nanowires [13] may shed some light on what is occurring with the synthesis of InGaAs wires. It has been shown that with Au-seeded InAs wire growth, when the In-Au reach a growth temperature above their eutectic point, nanowire growth ceases. It is possible that the ternary alloy of InGaAs has a liquid phase temperature at or below the growth temperature of 460 °C which could prevent InAs precipitation from the Au colloid. More experimentation and analysis, such as HR-TEM, EDS and other spectroscopy, needs to be completed before the Au-InGaAs system will be fully understood. Further analysis will be completed in the future.

3.4 Off-Cut Samples

Altering the surface of the substrate can have notable effects on nanowire growth. This is especially important for planar nanowires as they interact with the substrate along the entire length of the wire, in contrast to vertical wires which only interact at their base. To illustrate this, we grew nanowires on substrates that were off-cut 10° towards the [1-10] direction; the results are outlined in Figure 3.9. Normally, planar wires grow parallel in either the [01-1] and [0-11] directions. Once grown on the off-cut sample, they exhibit angled growth trajectories that differ from their normal paths and are no longer parallel. The normally [01-1] wires grow ~10.19° off-angled while the [0-11] wires are ~8.16° off-angled, and both are rotated away from the off-cut direction. Planar nanowires have been observed intersecting, as in Figure 3.9, which does not

occur normally on (100) substrates; this could lead to interesting device possibilities. The nanowires also appear to be rotated on their own axis, which reveals new crystal facets along their growth direction. The fact that the wires rotate towards the same direction, combined with the results of other studies [14] on substrate orientation concerning nanowire growth, leads to the possibility that there could be an orientation where the nanowires all align in the same direction or even cross each other perpendicularly, which could potentially be utilized in future devices. This is extremely important as aligning nanowires is non-trivial and is currently an active area of nanowire research.

3.5 References

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3.6 Figures

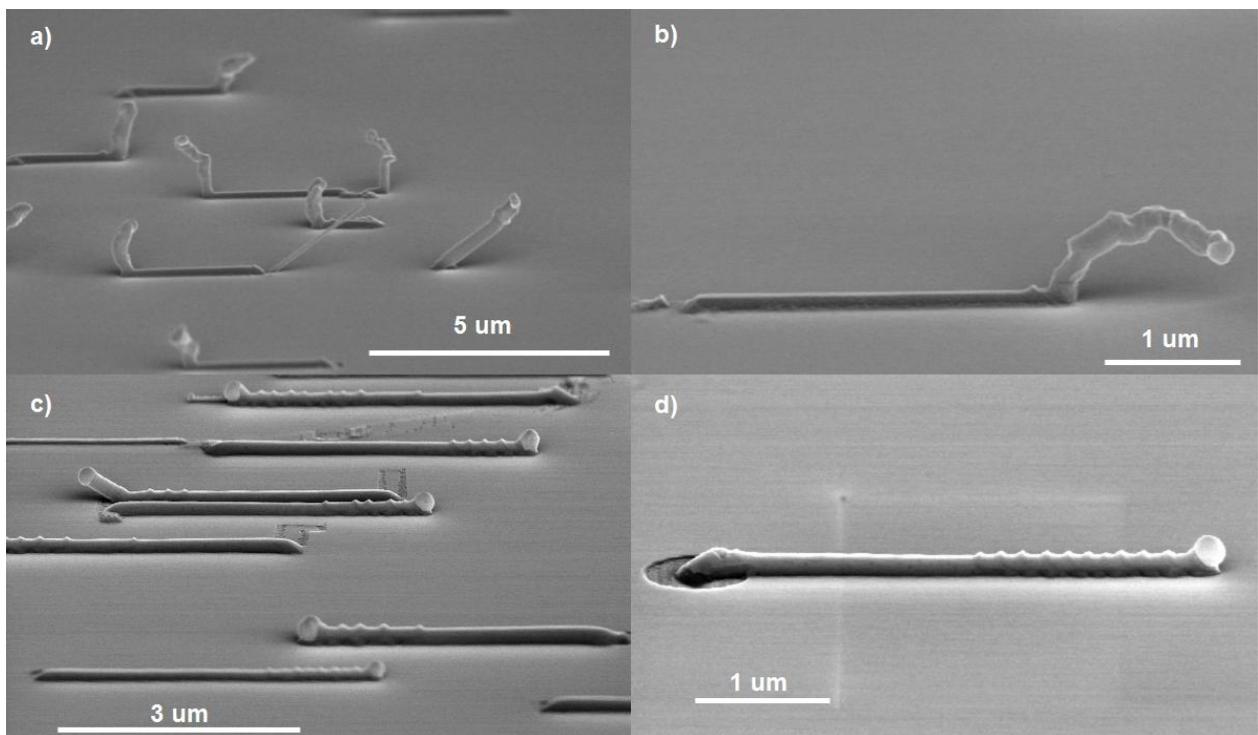


Figure 3.1. SEM images from a two-step growth where Zn source is turned on halfway into the nanowire growth, with a gas phase Zn/Ga molar ratio of (a) 1.6×10^{-2} zoomed out, (b) 1.6×10^{-2} view of a single nanowire, (c) 8×10^{-5} zoomed out, (d) 8×10^{-5} view of a single nanowire.

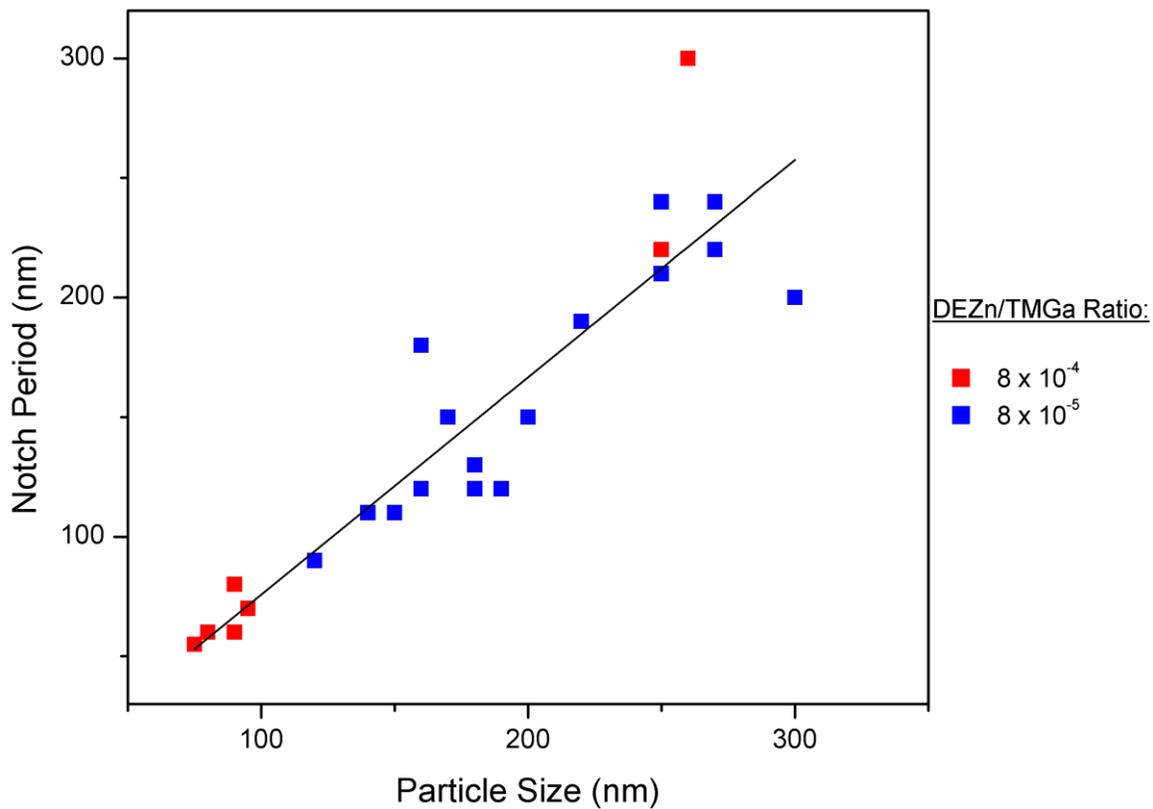


Figure 3.2. Plot of the notch period in Zn-doped planar nanowires as a function of Au catalyst particle size, from two doping levels (Zn/Ga ratio) as indicated. The solid line is the best linear fit to the data with a slope of 0.91, indicating a strong correlation between the notch period and the catalyst particle size.

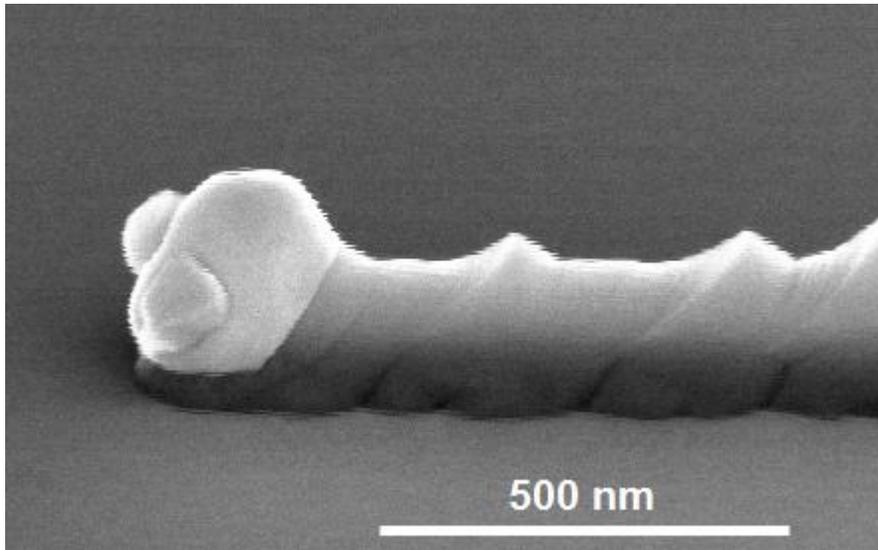


Figure 3.3. SEM image showing solid precipitants (presumably Zn; see text) on the surface of the Au seed particle in a moderately Zn-doped planar nanowire. The particulate is more prevalent with increasing Zn/Ga gas phase ratios.

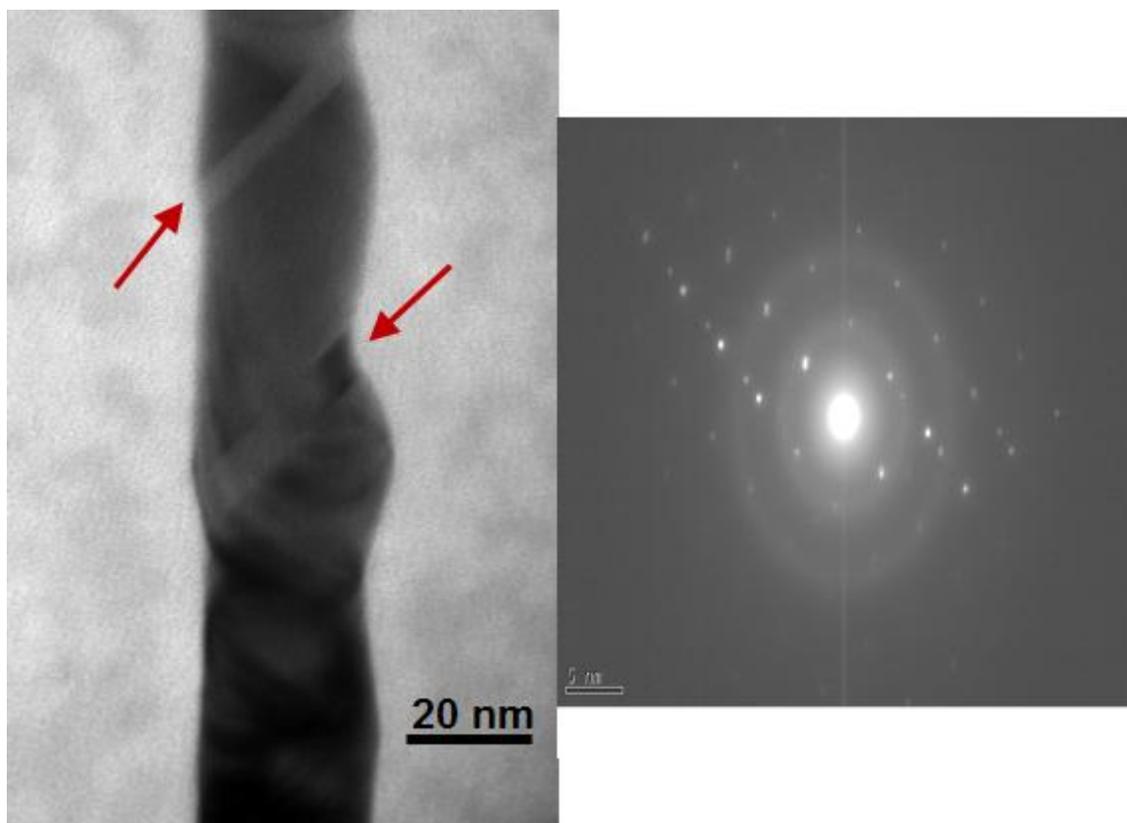


Figure 3.4. Left: A bright-field TEM image showing twin boundaries in the nanowire. (The growth direction of the nanowire is along $[110]$, while the twin boundary is in the (111) plane.) Right: Selected-area electron diffraction pattern along the $[110]$ zone axis of the nanowire showing the existence of twin boundary.

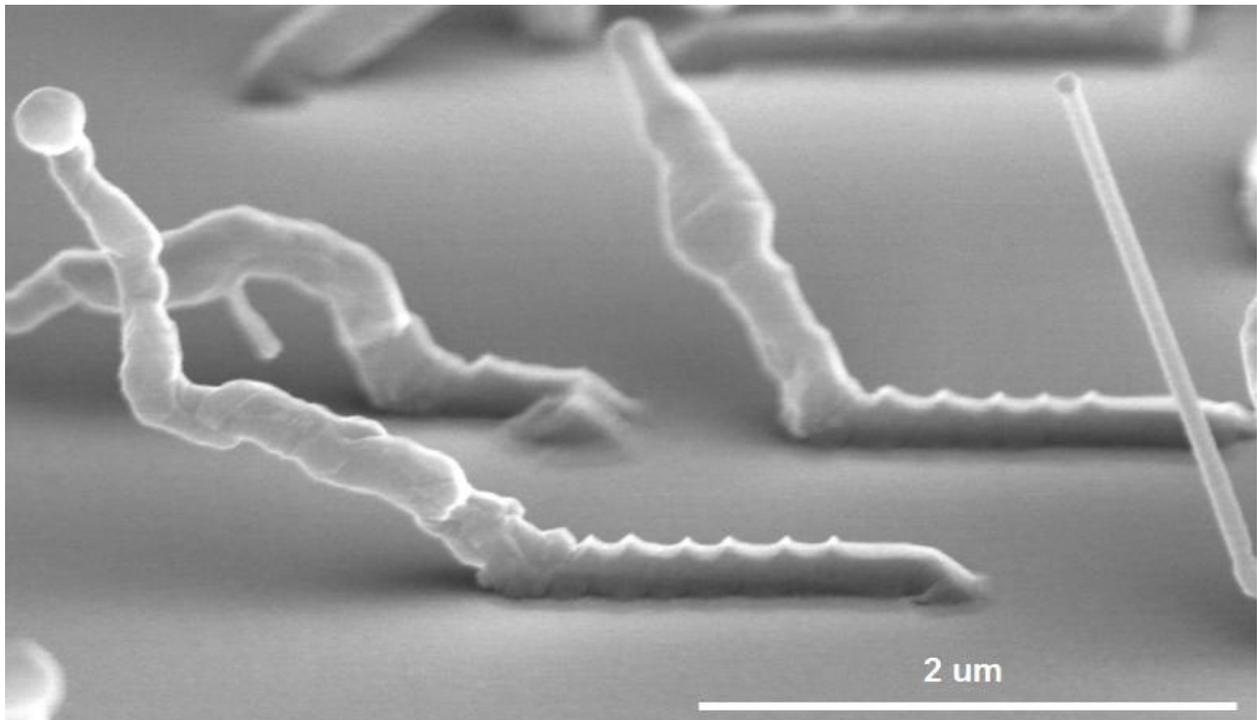


Figure 3.5. SEM image of Zn-doped GaAs nanowires from a single step growth with constant Zn/Ga gas phase ratio of 8×10^{-4} . Nanowire morphology changes from a periodic notching planar structure, followed by an incoherent off-plane configuration. The brief, smooth planar segment ($\sim 0.4 \mu\text{m}$) at the beginning had no Zn present.

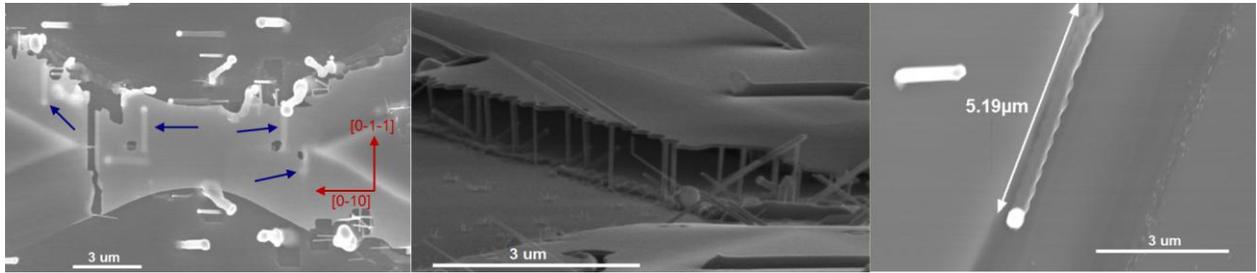


Figure 3.6. Observations of planar nanowire growth on suspended films. (a) We observed nanowire growth in perpendicular $\langle 110 \rangle$ directions that do not normally occur on standard (100) bulk crystal substrates. (b) Nanowire growth that extended vertically toward the substrates, then switched direction as the wires came in contact with the surface. (c) Planar nanowire growth that was modulated along a step height switching between different $\langle 110 \rangle$ directions.

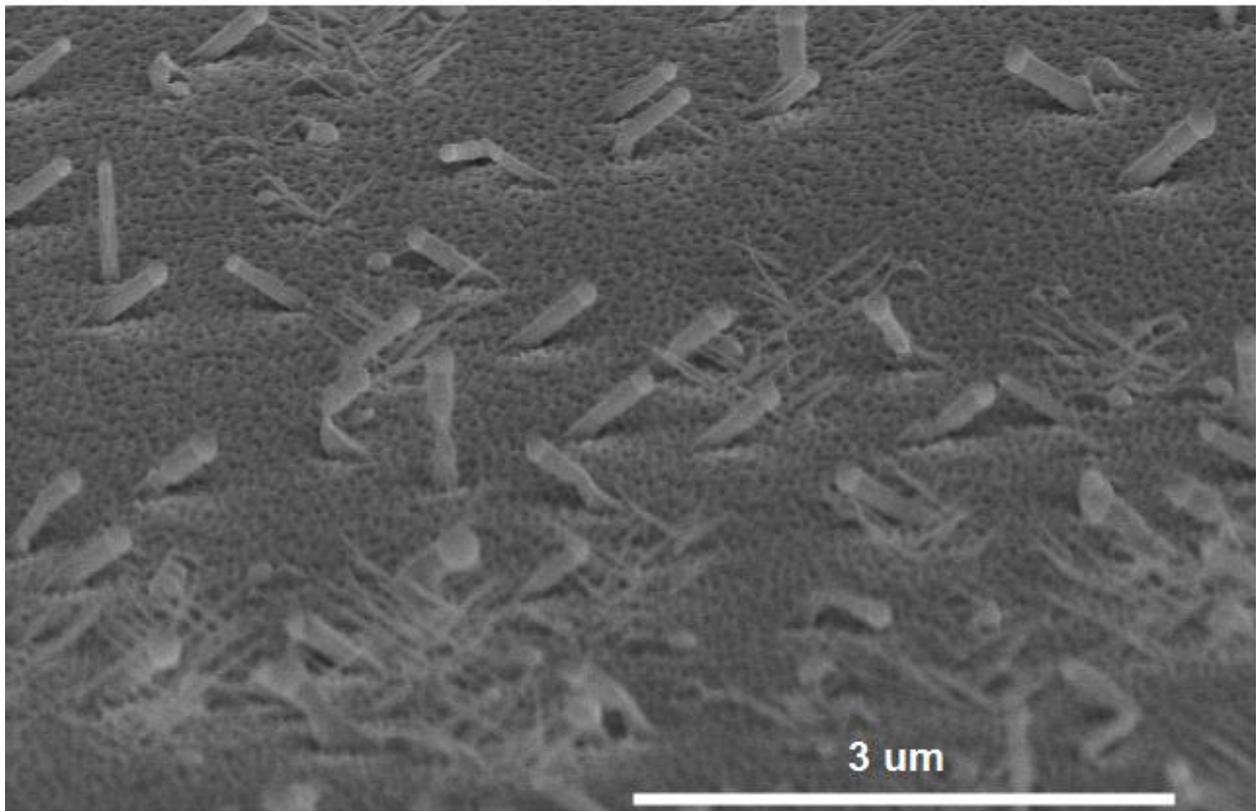


Figure 3.7. Nanowires grown with a flow rate of TMI and TMGa that would be equivalent to $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$. Note the overgrowth on the surface and the stunted nanowire growth.

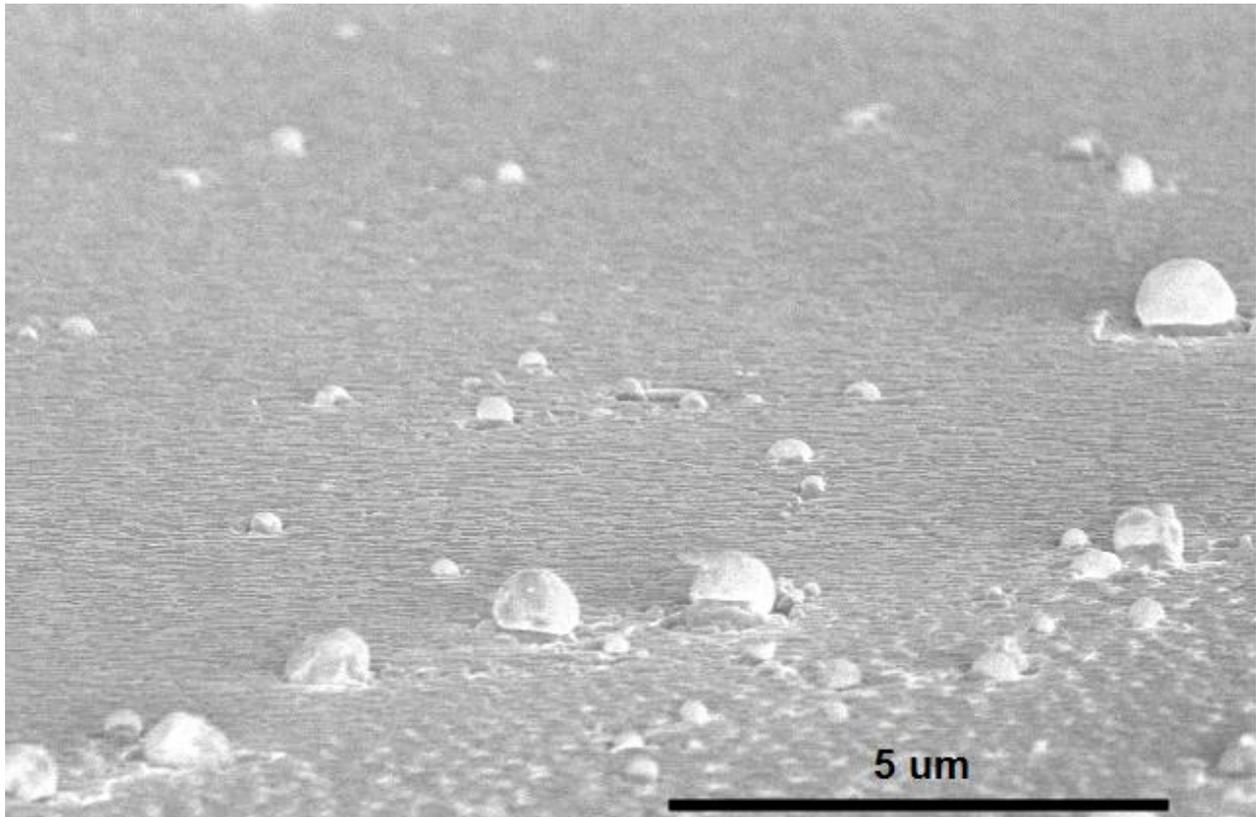


Figure 3.8. Nanowires grown under the conditions for an InAs layer. There is a lack of nanowire growth and significant growth on the surface.

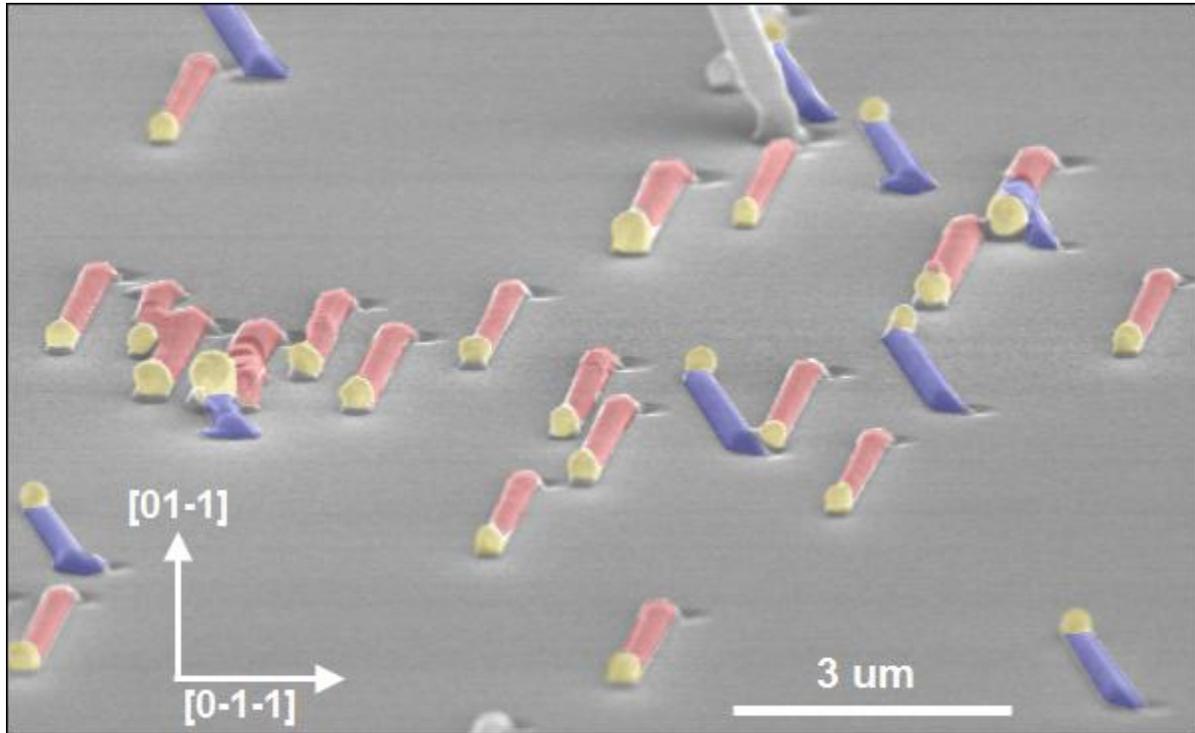


Figure 3.9. SEM image of planar GaAs nanowires grown on a substrate off-cut by 10° towards the $[1-10]$ direction. The nanowires self-align in two orientations as highlighted.

4. QUANTUM DOTS

4.1 Quantum Dots

Semiconductor devices are constantly being scaled down further and further. Aside from increased device density, there is another benefit as new characteristics reveal themselves with reduced dimensions. As devices scale down, so do their available energy states. When the size of the device approaches the De Broglie wavelength of an electron, the density of available energy states sharpens and ceases to behave like a quasi-continuum as in the case of bulk 3D crystals. If the device is confined in one dimension, a quantum well, density of states behaves like a step function with constant number of available states per subband. Further confined in another dimension, a quantum wire, the available states follow $E^{-1/2}$ where E is the energy of the carrier. Finally, when the device is confined in all three dimensions, a quantum dot, the density of states becomes a set of discrete states resembling a delta-function at specific energies. The sharpening of the energy states implies that it is possible to produce devices that operate at different wavelengths simply by varying the size of the quantum dots. This has important ramifications for optical devices such as photon detectors, lasers, LEDs and other optoelectronics. By varying the materials, the substrate, and the growth conditions, a variety of novel nanostructures can be produced for both fundamental studies of quantum confined systems, and for advanced photonic devices.

Although quantum dots are a heavily researched field and hold much promise to become an industry staple, they do have some shortcomings. Since quantum dots generally have a small volume, their emission and absorption tend to be weaker, so they have to be fabricated in high densities but without aggregating into large clusters which no longer have the energy

quantization properties. In order to create discrete quantum dots but in high enough densities to be useful, a method called strain-induced self-assembly is utilized [1]. This method depends not on lithographic techniques, which tend to be problematic and expensive at such small dimensions, but rather on heteroepitaxy. The detailed growth method of the quantum dots is explained further in the experimental section of this thesis.

III-V heteroepitaxy has been the traditional route for self-assembled III-V quantum dots (II-VI quantum dots are mostly formed by solution based colloidal synthesis) [2]. The direct bandgap, tunable lattice mismatch, and wider selection of materials make it a robust system for this type of growth. There are issues that make it less attractive for broad commercialization: III-V materials, when compared to silicon, have much higher material cost, and long-term investment may be an issue due to the rarity and uncertain future availability of indium and gallium in the Earth's crust [3, 4]. Most of the cost is in the substrate, which provides necessary functionality to the quantum dot systems. For example, for self-assembled InAs QDs on a GaAs substrate, the dots themselves are the active device while the substrate provides a quantum confinement barrier and the strain necessary for the self-assembly to occur. The function that the GaAs provides could potentially be provided by other substrates, but the caveat is that the substrate has to provide the correct amount of strain. With too little strain, the dots coalesce into a continuous layer, while with too much strain, the dots are incoherent with crystal defects. These defects can act as traps for carriers and degrade the quantum efficiency of the device.

Recently, suspended membranes have been investigated as a potential solution to some of the economic issues with self-assembled quantum dots. Fabrication of suspended thin silicon membranes is outlined in the experimental section of this thesis. Researchers have discovered unique phenomenon when strain-mismatched Ge quantum dots were grown on thin Si

membranes [5]. Remarkably, the strain interaction with the thin membrane naturally orders the dots in a continuously alternating fashion with one dot on the top and one on the bottom of the membrane, as shown in Figure 4.1. As a secondary effect, this causes the film to undulate, with QDs atop the crest and at the bottom of the trough. The interaction between the dot and the membrane shows that the thin membrane is very compliant and will adjust readily to accommodate the strain of the quantum dot since there is no restoring force on the thin membrane as with a bulk substrate. The degree of compliance is supposed to be larger than for solid films, which should lead to the possibility of producing quantum dot materials on membranes that would normally cause dislocations or metamorphic growth on bulk substrates. III-V materials were chosen as the perfect candidate to test this hypothesis as the lattice mismatch between GaAs and Si is similar to Ge and Si, and InAs on Si provides a much larger mismatch than elemental Ge on Si. It will also be of interest to verify that the dots could possibly align themselves for material systems in general, as in the case of Ge QDs on Si membranes. GaAs quantum dots were grown on silicon membranes at various growth conditions to gauge the effect of different growth parameters on the quality of the quantum dot produced. Coverage, growth interruption, and temperature were chosen as the parameters to vary independently.

4.2 Effect of Coverage

Coverage, referring to the number of intended monolayers grown by adjusting precursor flow rates and growth time, is an important parameter to consider when growing quantum dots. The amount of coverage dictates the growth mode. At low coverage, growth either forms 2D islands, similar to Frank-van der Merwe growth modes, that do not have enough material to aggregate into quantum dots, or forms some dots that are at too low of a density to be useful. At

high coverage, dots will become incoherent in order to reduce the intrinsic strain by creating dislocations instead of forming a pseudomorphic interface. At very high levels of coverage, the dislocated dots form in extremely high densities and can amalgamate into thin metamorphic films. The type of materials system determines which coverage range produces highest quality quantum dots.

Figure 4.2 shows the effect of coverage on the size and density of GaAs QD growth suspended silicon membranes at a growth temperature of 450 °C, with a constant flow of 5 sccm of TMGa at growth times of 2 s, 4 s and 20 s. There is a direct relationship between density, size and the appearance of QDs that are abnormally large compared to other QDs. These large QDs are possibly formed from increased Oswald's ripening due to the larger amount of precursor present at higher coverage. However, no difference between the growth on suspended membranes and supported silicon films has been observed at all coverages under the specified growth temperature.

4.3 Effect of Growth Interruption

Growth interruption is essential in the growth of QDs in order to create coherent and dislocation-free quantum dots. This is achieved by interrupting the flow of precursors while keeping the H₂ carrier gas and maintaining constant growth temperature. The interruption allows time for material to diffuse, coalesce and form proper Stranski-Krastanov quantum dots. In arsenic based crystals that use arsine as their hydride for an As precursor, this is especially crucial. Heinrichsdorff et al. have done research on the effect of AsH₃ post-dot formation before the chamber is cooled down [6]. They found that the hydrogen radicals from the arsine molecule would cause defects in their InAs quantum dots. The best solution they found is to actually turn

off arsine flow during their growth interruption, which resulted in higher quality dots. Excess arsine in the growth chamber, which is not necessary for growth and the prevention of out-diffusion of As from the substrate, is limited to prevent hydrogen incorporation, making low V/III ratio a priority. The effect of GI time on the QD quality is hard to quantify using microscopy and is usually done with spectroscopy methods [7]. Spectroscopy measurements will be carried out in the future for this project. GI time was varied from 30 to 90 s and no apparent physical differences have been observed between dots grown on the suspended membrane and those on supported silicon film.

4.4 Effect of Temperature

Temperature controls multiple aspects of QD growth, and is one of the most important parameters to consider when growing QDs on suspended films. Temperature affects the crystal growth in general as well as QD formation. In MOCVD, different precursors pyrolyse, or crack, under different temperatures, which causes their pyrolysis efficiency to change with temperature. Hence it is possible to get increasing coverage from the same flow rate of precursor simply by increasing the temperature. Secondly, some materials tend to be more diffusive at higher temperatures than others. This is important when using indium in quantum dot growth. Indium has a tendency to be extremely mobile and segregate at higher temperatures [8]. Material also tends to diffuse farther at higher temperatures, leading to naturally larger quantum dots. For GaAs QD growth on silicon membranes, an interesting phenomenon has been observed when the growth temperature is varied. Figure 4.3 shows the SEM images of GaAs QDs grown at 625 °C and 800 °C on a ring-shaped silicon substrate with suspended membranes at the edges and the supported part in the middle. It can be seen that QDs selectively grow on the suspended

membrane (appear to be on the backside), with hardly any growth on the supported silicon substrate. With further increased temperatures, QD growth maintains its preference of the membrane while combining into large chunks, probably due to higher diffusivity and increased Oswald's ripening. In contrast, the QDs shown in Figure 4.2 were grown at 450 °C and no selectivity was exhibited between suspended and supported substrates.

The selectivity observed is most likely a result of increased mobility/diffusivity of precursor materials at higher temperature. The tendency of QDs to grow on the backside of the membrane could possibly be due to the larger number of nucleation points underneath of the suspended edge, as it was the Si/SiO₂ interface before released. The exact mechanism is not entirely known at this time and is under investigation. The preferential growth location leads to the possibility of making selective area growth using suspended regions to pattern QDs indirectly.

In summary, no ordering has been observed under all the conditions explored so far for the growth of GaAs quantum dots on silicon membranes. The only difference from bulk silicon substrates appears at high growth temperature, where preferential growth on the suspended part occurs. Further exploration of III-V quantum dots on suspended silicon membranes will include the growth on thinner (< 13 nm) membranes, continued optimization of growth conditions, and InGaAs QD growth. Ordered III-V quantum dots on silicon could be candidates for room temperature thermoelectric Si-based nanosystems with discrete minibands [5].

4.5 References

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4.6 Figures

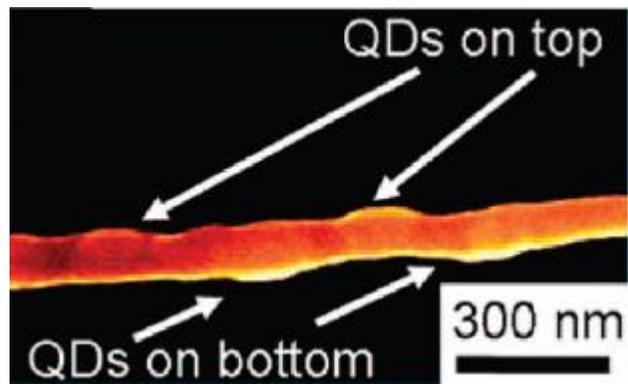


Figure 4.1 Quantum dots on the top and bottom of a suspended silicon membrane. The spacing between the dots is ~ 350 nm [4].

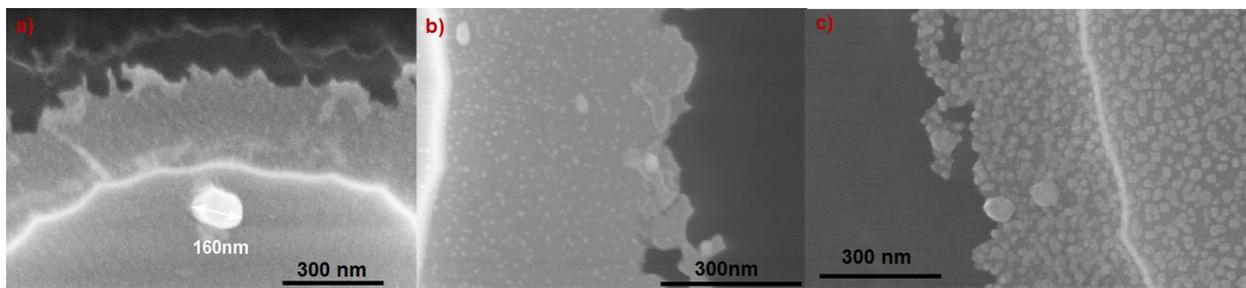


Figure 4.2 SEM photos showing the effect of coverage on GaAs quantum dots grown on suspended silicon membranes. At 1.65 ML the dots are barely visible under SEM (a), while at 3.3 ML (b) the dots are more pronounced and clearly visible. At high coverages, 16.5 ML (c), the dots start to become larger and denser, beginning to merge with one another.

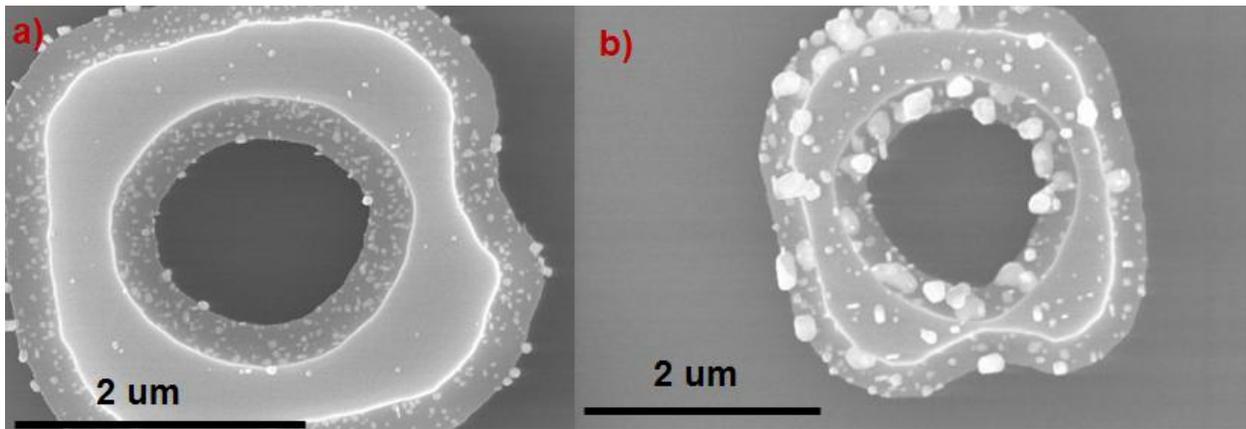


Figure 4.3 SEM photographs showing the selective quantum dot growth on suspended membranes at higher temperatures. Grown at 625 °C (a) the dots prefer to grow on the suspended membranes. At 800 °C (b) the dots still prefer to grow on the edge and larger chunks begin to appear.

5. CONCLUSION

5.1 Summary

The phenomena associated with incorporating Zn, growing on suspended membranes and 10° off-cut substrates with VLS planar $\langle 110 \rangle$ GaAs nanowires have been investigated. Nanowires that have been grown with DEZn present have produced alternating twin planes in the $\langle 111 \rangle$ crystal direction that have controllable period lengths roughly correlated to the size of the catalyst particle. Planar nanowires grown on suspended membranes reveal new growth directions that are not apparent on bulk substrates. Planar GaAs nanowires usually grow in the $[0-11]$ and $[01-1]$ crystal directions but appear to grow in $[011]$ and $[0-1-1]$ only on GaAs suspended membranes, which could be used for alignment and for planar nanowire arrays. Planar nanowires grown on 10° off-cut samples exhibit asymmetrical rotation away from the off-cut direction. The asymmetrical rotation shows the possibility of creating wires that could face all one direction or cross at specified angles, which could be useful in creating devices that would require such specifications.

III-V self-assembled quantum dots on suspended thin silicon membranes are being investigated as a possible solution to the integration of compound and elemental semiconductor materials. Controlling aspects of growth using coverage, growth interruption and temperature, as well as their effects, have been studied. Coverage has been shown to influence quantum dot size and density, while growth interruption effects, while having no external features, should prove useful in the creation of high quality dots once the optical analysis phase of the study begins. Temperature has shown the largest effect by not only controlling QD size and density, but also exhibiting influence over selective area growth,

leading to the possibility of patterning QDs where lithographic techniques can not be used effectively.

5.2 Future Directions

In addition to the interesting crystal phenomenon associated with Zn-doped planar $\langle 110 \rangle$ GaAs nanowires, there is a bevy of potential electronic and optical applications suited for such a structure. Theoretically there has been speculation about the possibility of minibands [1] and carrier tunneling naturally occurring due to the highly periodic structure of the nanowire twin formation [2]. Preliminary on-substrate electrical measurements have been performed with the Zn-doped nanowires. The tests revealed an abnormally leaky substrate that made it impossible to probe individual nanowires. Control experiments done on undoped nanowires showed very low electrical leakage, pointing to the dopant as the culprit. Future experiments will be done to try to encourage Zn incorporation only into the nanowire itself, and to limit diffusion into the substrate. If this is not attainable, methods to circumvent the substrate, such as removing the nanowire from its host or suspending it over air to create insulation, will be investigated.

The inclusion of indium in GaAs nanowires will be very beneficial in the future of planar wires to widen the possibility of potential devices. Preliminary results show there is little indication of indium incorporation in initial experiments. More trials need to be completed, although V/III ratio [3] and growth temperature may play important roles in how indium is incorporated in the wire, especially when considering the results of a study on vertical InAs wire growth [4]. Wires grown on suspended films exhibit how accommodating planar nanowires are to their substrate as well as how much of a role substrate plays in their

growth. Different types of substrate growth conditions are being looked into, such as the role of thickness in suspended membrane nanowire growth and how various types of obstacles affect growth such as barriers, pits, gradual slopes and abrupt changes in crystal planes. Lastly, research on planar nanowire growth on off-cut substrates is being furthered. Substrates of various degrees of off-cuts and different orientations are being examined to learn whether one can grow nanowires in a desired direction, or at the least eliminate the dual growth direction and have only one direction available to improve their alignment in future devices.

The next steps in the study of self-assembled QDs on suspended silicon membranes will be to complete the study of all the growth parameters on QD formation. Parameters such as deposition rate, material composition and membrane thickness will be adjusted to observe any ordering besides the already observed selective area growth. Once all the parameters are observed, those that prove to create the highest quality dots will then be tested with more thorough metrology, such as TEM and spectroscopy, in order to gauge their quality. TEM will be useful to observe any crystalline defects, while spectroscopy tests will prove beneficial to determine their optical characteristics.

5.3 References

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