



Growth of Group III-V Nanowires using Nanosphere Lithography, Vacuum Evaporation, and MOCVD

Prepared by:
Daniel Wells

Faculty Advisors:
Dr. Michael West
REU Site Director, Department of Materials and Metallurgical Engineering

Dr. Phil Ahrenkiel
Associate Professor, Nanoscience and Nanoengineering Program

Dr. Alfred Boysen
Professor, Department of Humanities

Program Information:
National Science Foundation
Grant NSF #1157074

Research Experience for Undergraduates
Summer 2013

South Dakota School of Mines and Technology
501 E Saint Joseph Street
Rapid City, SD 57701

Table of Contents

Abstract	3
Introduction	4
Broader Impact	4
Procedure	5
Materials.....	5
Equipment.....	5
Nanospheres.....	6
Vacuum Evaporation.....	6
Dissolve the Spheres.....	7
MOCVD Process.....	8
Results	9
Nanosphere Lithography.....	9
Hexagonal Arrays of Catalyst Droplets.....	17
Nanowire Growth.....	18
Discussion	29
Conclusion	32
References	34
Acknowledgments	36

Abstract

The MOCVD (metal organic chemical vapor deposition) growth process of nanowires has a strong potential to be used to produce nanowires suitable for use in photovoltaic applications. This process essentially builds nanowires from the bottom up, working at the atomic level. The procedure used for growing nanowires using the MOCVD process involves several steps. First, nanosphere lithography is used with polystyrene spheres with diameters between 356 and 540nm to create a hexagonal pattern on substrates consisting of carbon coated copper and molybdenum grids with a carbon film, as well as on gallium arsenide (111)B substrates. Next, vacuum evaporation is used to evaporate a catalyst – gallium – onto the pattern of spheres. Then, the spheres are dissolved using chloroform, leaving behind a hexagonal pattern of gallium droplets. Finally, the MOCVD growth process itself is used to attempt to use the catalyst (the gallium droplets) to grow nanowires consisting of gallium arsenide using the VLS (vapor-liquid-solid) method.

Early results revealed the difficulty in producing the correct conditions to actually grow nanowires in the MOCVD system. While achieving a hexagonal array of the catalyst and achieving growth of gallium arsenide has been successfully demonstrated, no nanowires or nanowire-like objects were observed in this growth. Eventually, nanowires that were very long and narrow were able to be grown. However, even when this was accomplished, the composition of the nanowires still remained unconfirmed, and reproducing the wires turned out to be very difficult.

Introduction

Nanowires - very small wires that are approximately a few tens of nanometers in width – can be created in two general ways. The first is “top down,” which focuses on making larger objects smaller, down to the nano scale. The second is “bottom up,” which focuses on building the nanowires from essentially an atomic level. The latter is the method by which we attempted to build nanowires in this study.

One of the more common techniques for growing nanowires is using the vapor liquid solid (VLS) mechanism. The process by which we attempted to grow nanowires – MOCVD (metal organic chemical vapor deposition) uses this concept. Essentially, a catalyst is placed in a vacuum chamber and heated into the liquid state. Then, the materials that will form the nanowires are flowed in gas form into the chamber. The catalyst absorbs the materials, and, when it reaches saturation, nanowires begin to grow from beneath the catalyst droplets. In this study, copper and molybdenum grids with a carbon film are used as substrates to attempt to grow nanowires using nanosphere lithography with polystyrene spheres with a diameter between 356 and 540nm. Pure gallium is used in the vacuum evaporation process. It becomes the catalyst in the MOCVD process, where a growth of nanowires made from gallium and arsenic is attempted. Eventually, we would like to attempt to grow these nanowires on gallium arsenide (111) crystal substrates to achieve vertical alignment as well as patterned arrangement of the nanowires.

Broader Impact

Nanowires, if grown from group III-V Compounds, have semiconductor properties that render them suitable for uses in photovoltaic (solar cell) applications. Commercially available solar cells generally have efficiencies of around 20%, often even less. However, solar cells with

III/V compound semiconductors have reached efficiencies above 40% ^[2], which is an enormous step forward in solar-cell technology. If these kinds of efficiencies were widely available, solar cell practicality would increase dramatically. More than twice the amount of power could be gathered per unit area. However, efficiencies such as this are so far seen only in the laboratory. The research performed in this study explores methods and materials that can be used to create the nanowires that would be used in solar cells, especially wires arranged in a patterned and orderly fashion, which was attempted using nanosphere lithography, and wires aligned vertically, which was attempted by growing the nanowires on gallium arsenide (111)B substrates.

Procedure

Materials

Copper grids with 100 μm by 100 μm grid squares with a 200-mesh carbon film

Molybdenum grids with 100 μm by 100 μm grid squares with a 200-mesh carbon film

Pure gallium

Polystyrene nanospheres

Gallium in the form of trimethylgallium (TMGa)

Arsenic in the form of arsine (AsH_3)

Chloroform

Gallium arsenide (111)B substrates

Equipment

TEM – Transmission Electron Microscope

SEM – Scanning Electron Microscope

Note – There is a dedicated SEM in a separate building, the TEM has built in SEM capabilities.

Optical Microscope

Vacuum Evaporator

MOCVD system

Nanospheres

About 5 micro liters of a solution of water and polystyrene nanospheres was dropped onto the copper or molybdenum grids on the side with the carbon film, or onto gallium arsenide substrates, allowing the water to evaporate by letting it stand for at least 6 hours. The process can be slowed down if necessary. For the purpose of our objective, the nanospheres needed to form a mono or double layer of the hexagonal array. This is because, when the vacuum evaporator is used to evaporate the catalyst onto the sample, there needs to be space between the spheres for the catalyst to reach the copper or molybdenum plate/carbon film. If the nanospheres are thicker than two layers, then no such space will remain. The reason the nanospheres tend to form hexagonal arrays is because that is the lowest energy state between the spheres, since they can't be packed closer together. After completing the evaporation, the TEM and/or SEM was used to examine the substrates for hexagonal arrays of spheres.

Vacuum Evaporation

The samples, with nanospheres, were put into a vacuum evaporator. The vacuum evaporator works by melting and vaporizing a catalyst of choice in a vacuum which will condense and solidify on the samples. In our case, the catalyst was gallium. The machine sent a large current through a wire basket, causing the basket to heat up and glow, much like a light bulb filament.

The gallium, which was seated in the wire basket, first melted and then started evaporating. Our samples, placed upside down directly above the melting gallium, received a direct stream of gallium droplets. While the process can be monitored visually by watching the coating of gallium build up in the vacuum chamber, we chose to time the process to keep track of how much coating the samples received, coating them from 10 seconds up to 2 minutes, depending on our needs and the current through the wire.



Image 1: wire basket in vacuum evaporator



Image 2: vacuum chamber on the vacuum evaporator

Dissolve the Spheres

After getting a coating of gallium that was to our satisfaction, the nanospheres were then dissolved in chloroform to leave only the gallium that was actually attached to the substrate. This proved more difficult than we thought. An ultrasonic cleaner which was used (with the samples submerged in chloroform) essentially destroyed the carbon film and all the usable part of the sample. However, simply leaving the samples to soak in the chloroform yielded only small patches of the spheres that actually dissolved, even if they soaked for many hours, as if the gallium coating was protecting the spheres from the chloroform.

It was found that the effectiveness of soaking the spheres in chloroform depended greatly on the thickness of the gallium coating. Once a certain thickness is reached, most of the spheres don't dissolve, presumably because they are protected from the chloroform by the gallium. However, if the coating was too thin, then there would usually be insufficient gallium to form a hexagonal array of droplets. It was difficult to achieve the balance needed here, partly in due to the difficulty in controlling the evaporation rate in the vacuum evaporator. After the spheres were dissolved, the substrates were again examined using the TEM.

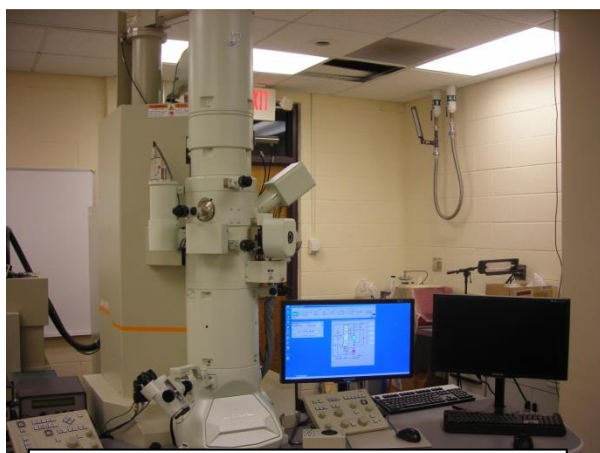


Image 3: TEM (Transmission Electron Microscope)

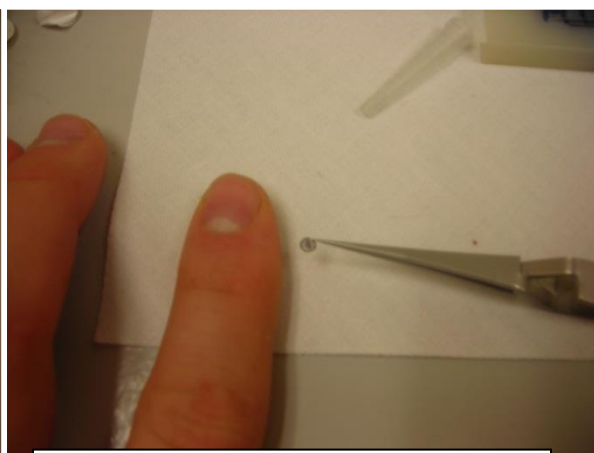


Image 4: Molybdenum grid positioned near a finger for size comparison

MOCVD Process

The MOCVD system itself has many potential leaks of gasses, and so is located in a room with a detector that monitors gas levels and alerts operators of the equipment if they reach potentially unsafe levels.

To use the machine, a tiny bit of colloidal graphite was used to secure the sample (copper or molybdenum grid) to a larger gallium arsenide substrate. This was then placed on the sample holder, which rotates at about 300 rpm during the process. The sample holder is placed under a

vacuum, and is heated using a coil of wire. This will melt the catalyst (in this case, gallium) to a liquid. Then, gallium and arsenic, in the form of trimethylgallium and arsine, were flowed into the chamber at rates and for time intervals that we believed would allow the growth of gallium arsenide (GaAs) nanowires.



Image 5: MOCVD System with MOCVD chamber pictured in center

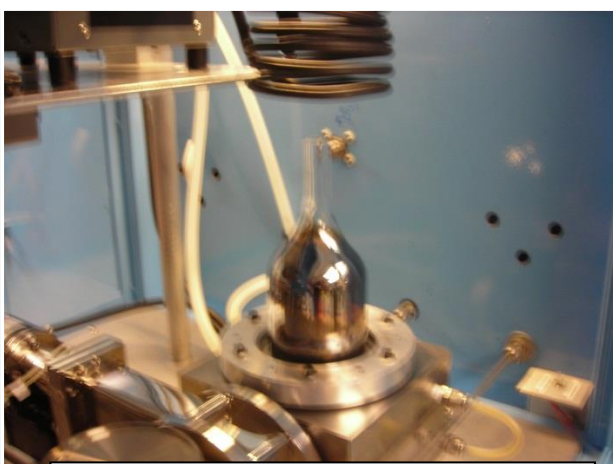


Image 6: Close up of MOCVD chamber

Results

Nanosphere Lithography

On our first four samples which used different diameter nanospheres, results varied. Spheres of diameter 540nm, 456nm, and 400nm all yielded hexagonal ordering (as well as square ordering, occasionally). However, all of them were inconsistent, with many regions that either were too thick to be useful or had no particular ordering at all. Additionally, spheres of diameter 356 yielded no hexagonal arrays at all, which is interesting considering the strong patterning of the 400nm sample.

When using the molybdenum substrates, the 540nm diameter spheres were the most consistent, so we started with only that size. The molybdenum yielded more consistent results than the copper, as there were large regions with usable patterned arrangements of spheres (Figure 5).

Additionally, nanosphere lithography was tried on solid gallium arsenide (111)B substrates. Initially, the substrates were used as they were, with no surface treatment (labeled “non plasma” in the images). After the results of these substrates were examined, the next samples were treated with plasma etching, which makes the surface more hydrophylic, hopefully resulting in the water diluted nanospheres spreading out more and forming more monolayers and less chunks. These images are labeled “with plasma.”

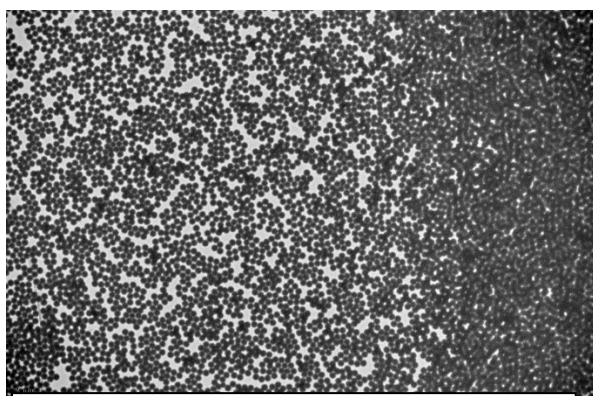


Figure 1: TEM copper 356nm – Mag x800
No hexagonal arrangement

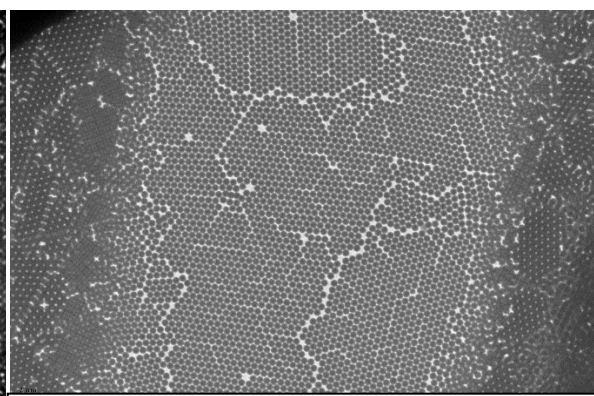


Figure 2: TEM copper 400nm – Mag x800
Hexagonally ordered nanospheres - monolayer

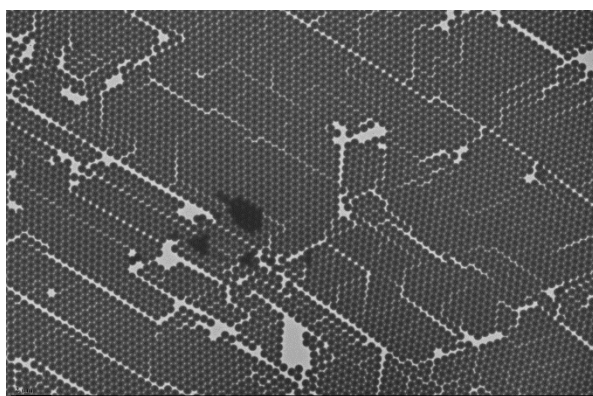


Figure 3: TEM copper 456nm – Mag x800
Hexagonally ordered nanospheres -
monolayer

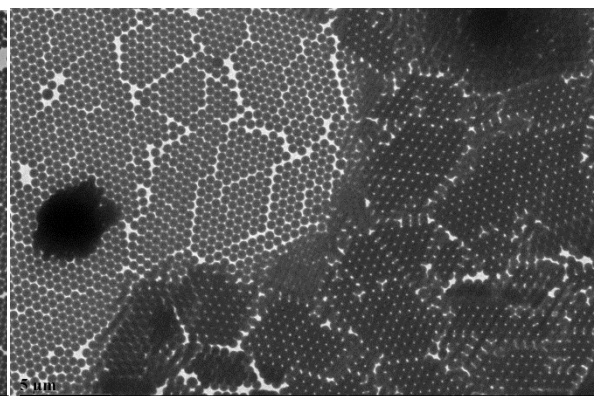


Figure 4: TEM copper 540nm – Mag x800
Hexagonally ordered nanospheres –
mono/double layer

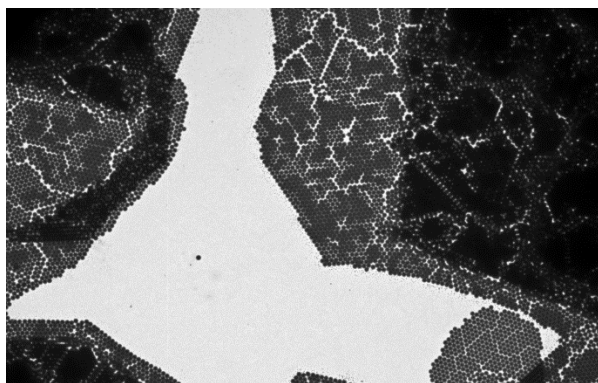


Figure 5: TEM molybdenum 540nm – Mag x400
Large regions of ordered nanospheres

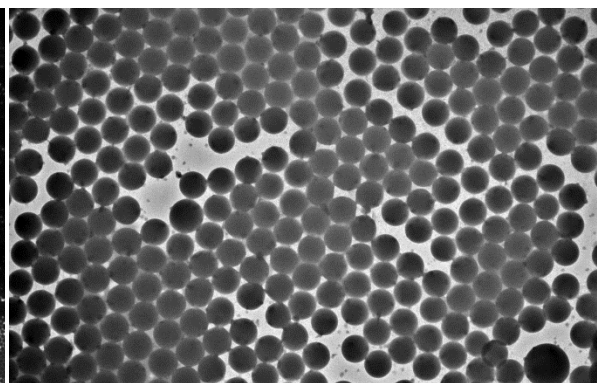


Figure 6: TEM molybdenum 540nm - Mag x2000
Close up of nanospheres

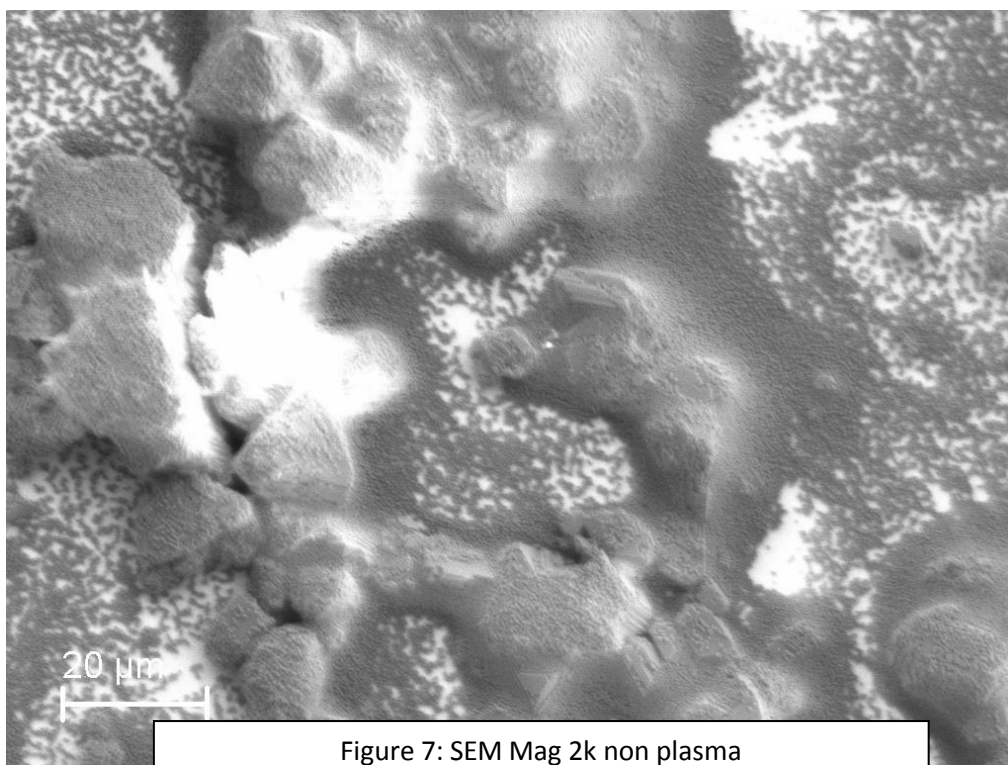


Figure 7: SEM Mag 2k non plasma
Large chunks of nanospheres

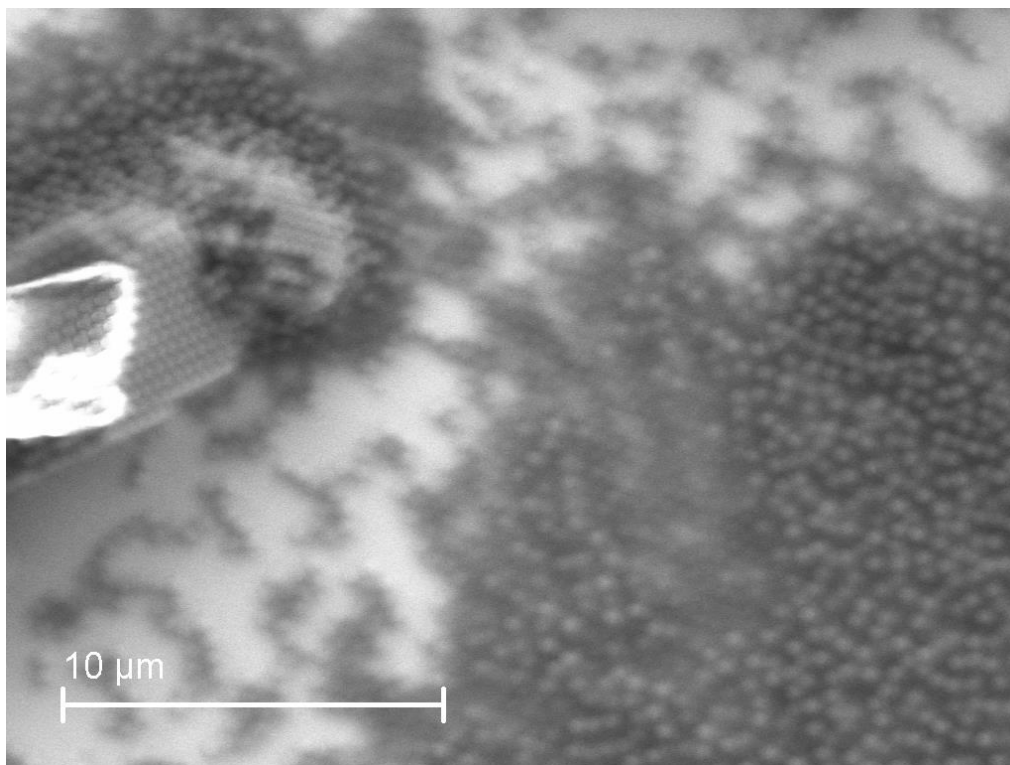


Figure 8: SEM Mag 10k non plasma
Ordered spheres in chunk, non-ordered everywhere else

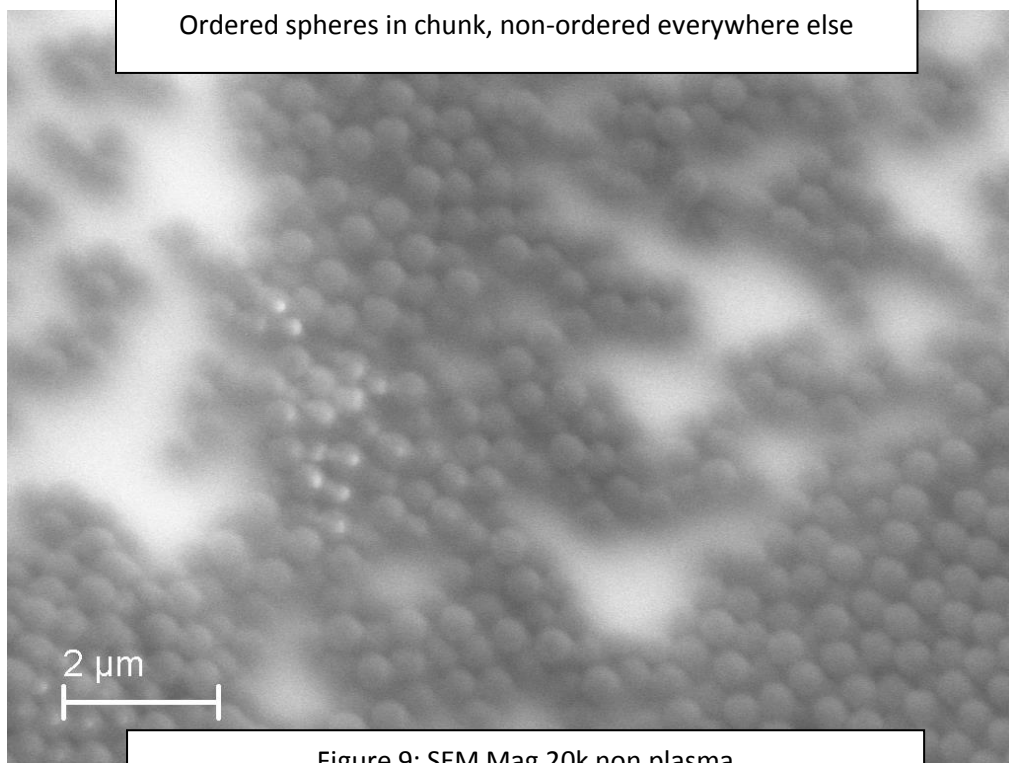


Figure 9: SEM Mag 20k non plasma
Mono/double layer – no ordered arrangement

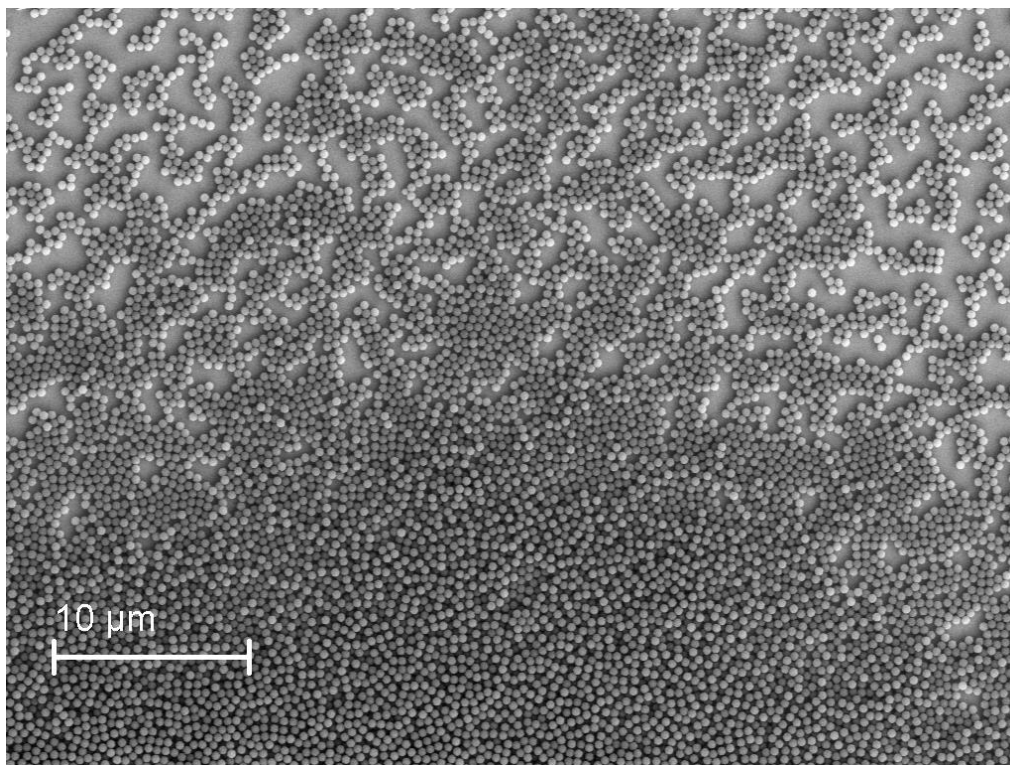


Figure 10: SEM Mag 5k with plasma
Mono/double layer – minimal ordered arrangement

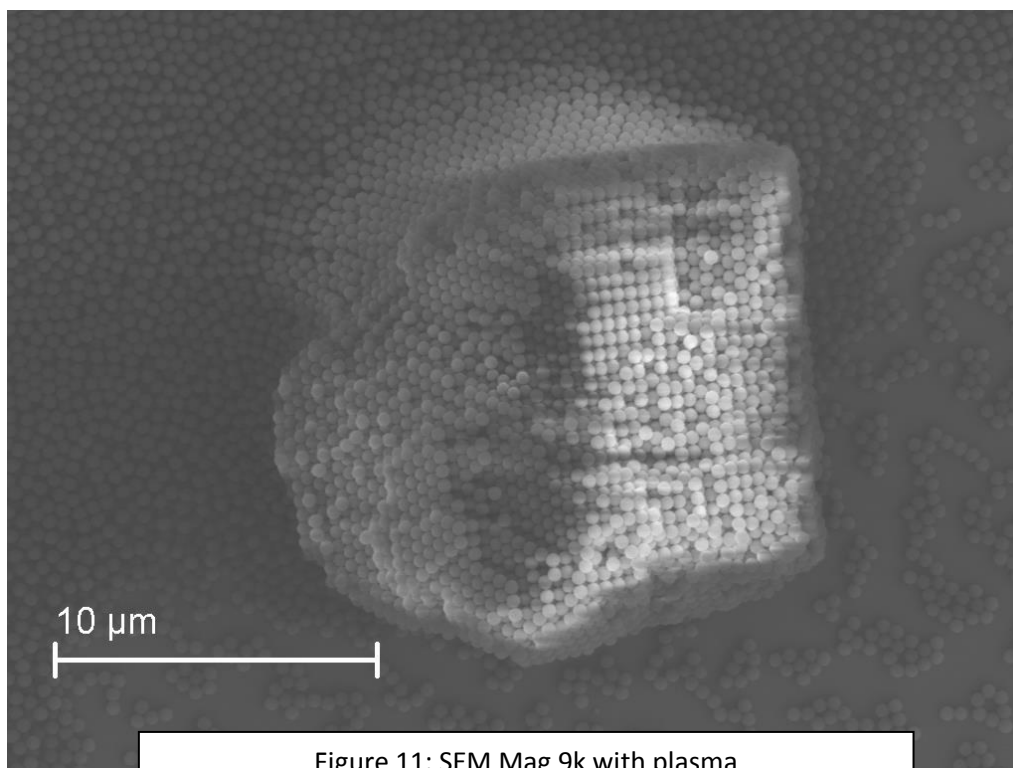


Figure 11: SEM Mag 9k with plasma
Large ordered nanosphere chunk

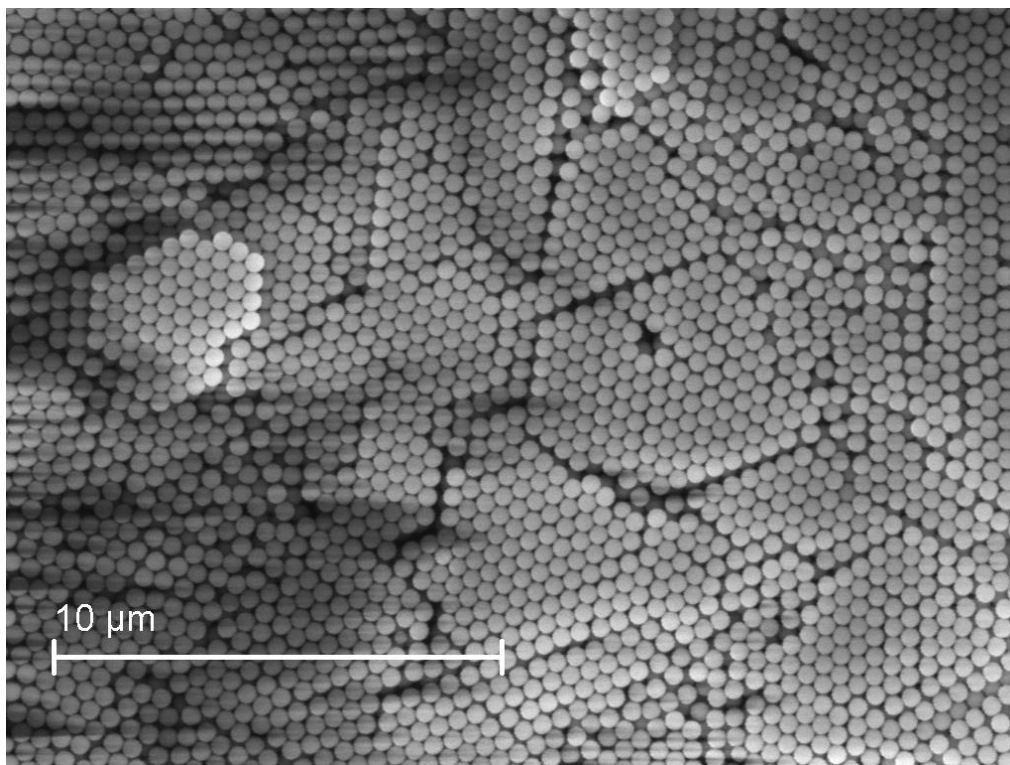


Figure 12: SEM Mag 12k with plasma
Ordered nanospheres; unknown number of layers

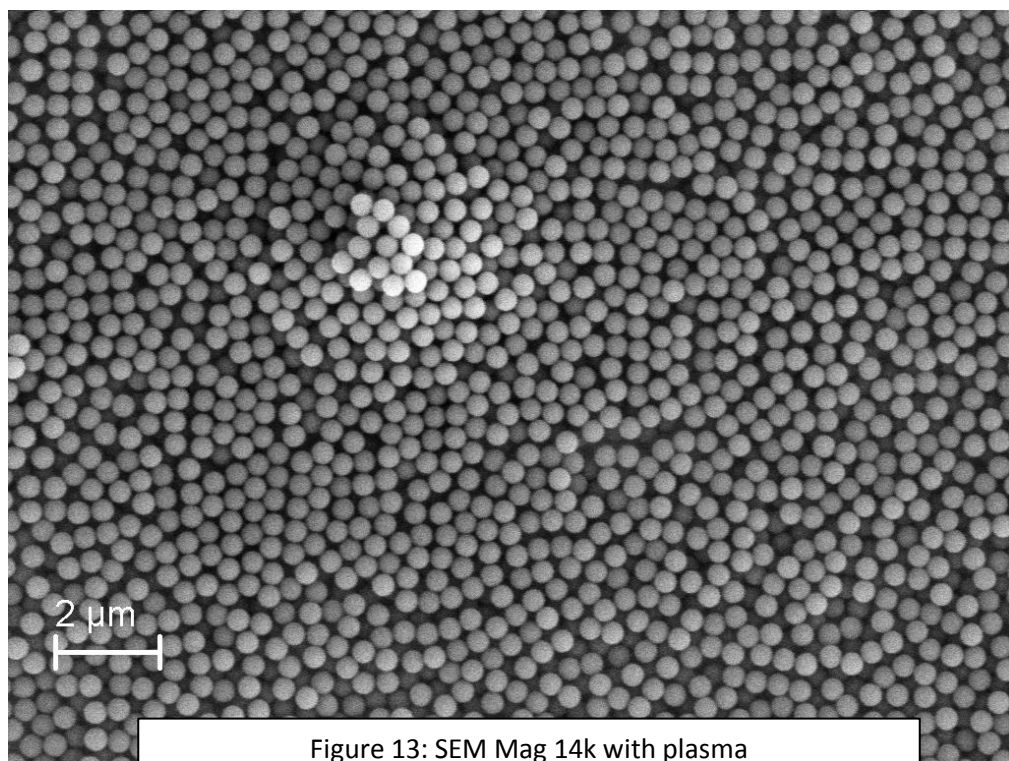


Figure 13: SEM Mag 14k with plasma
Minimally ordered nanospheres – common occurrence

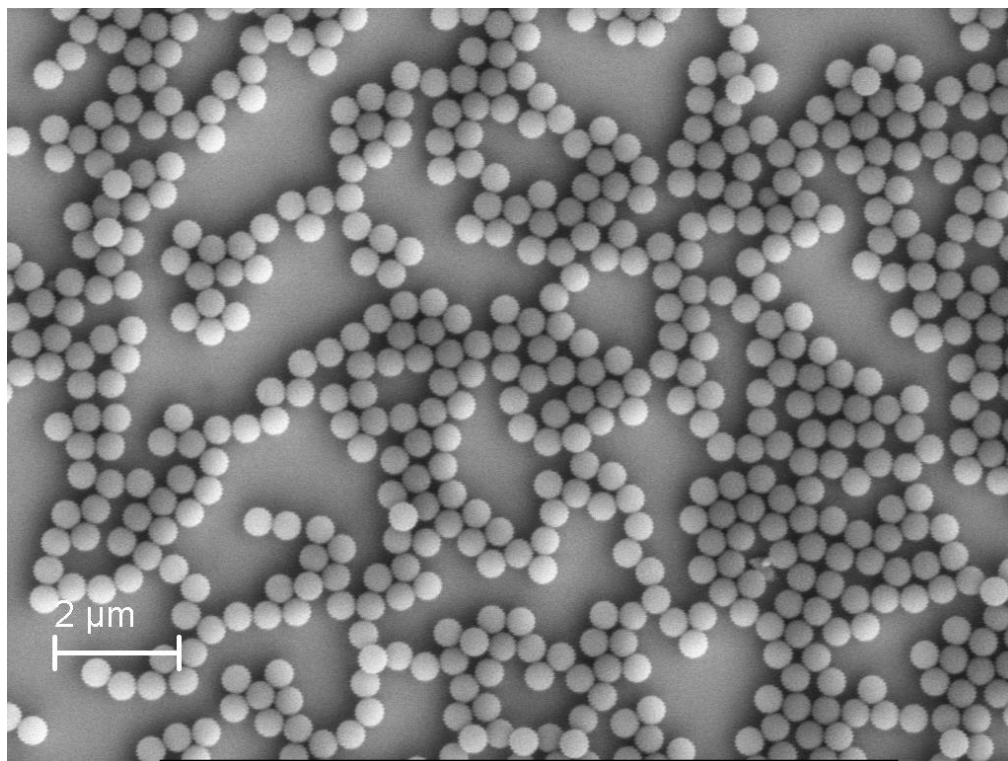


Figure 14: SEM Mag 17k with plasma
Non-ordered semi-monolayer – common occurrence

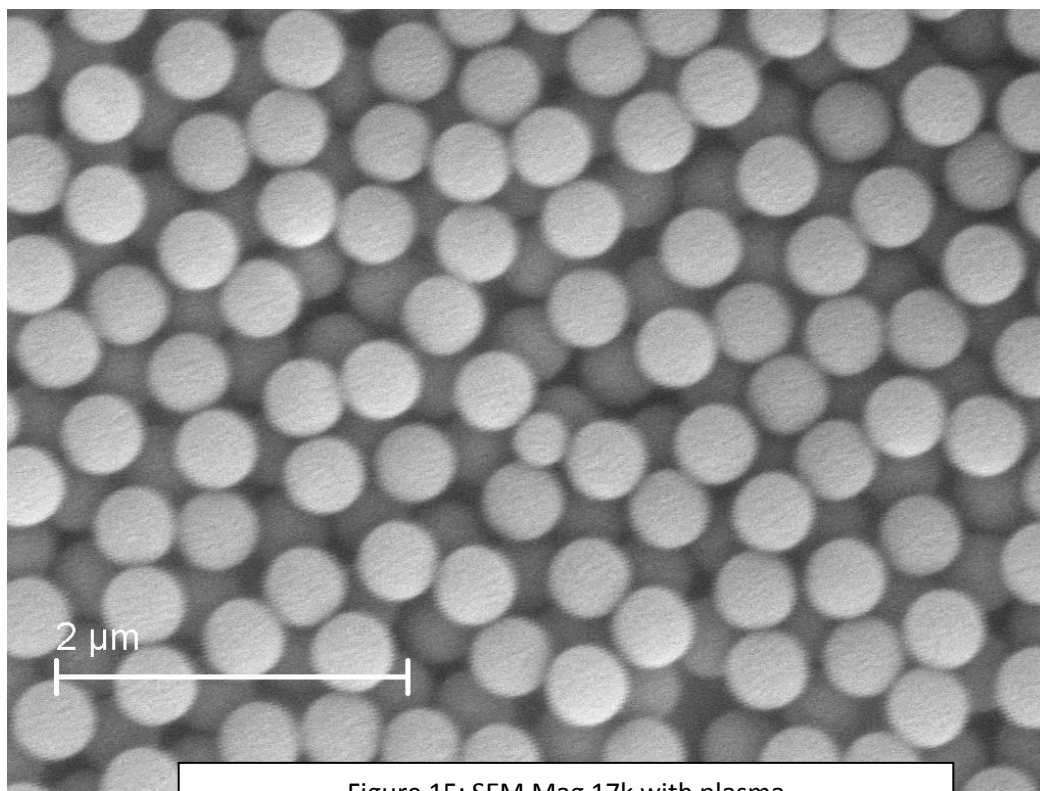


Figure 15: SEM Mag 17k with plasma
Non-ordered double layer

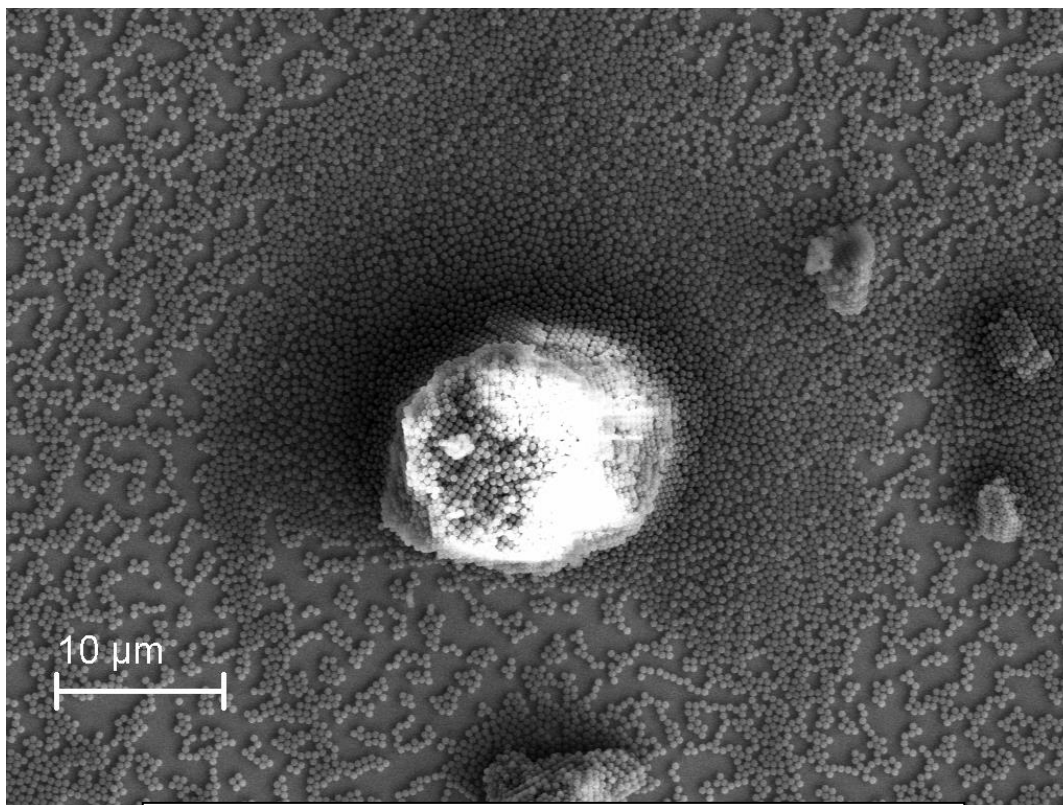


Figure 16: SEM Mag 4k with plasma
Large nanosphere chunk with visible monolayer surrounding it

Hexagonal Arrays of Catalyst Droplets

Of our initial samples on the copper plates, only two had any hexagonal patterning of the catalyst. The spheres of diameter 356nm were not used because they did not form any patterns. Initially we tried the ultrasonic cleaner on the 456nm because it was the least patterned of the three remaining samples. However, this completely destroyed any useful part of it. Consequently, we simply soaked the two remaining samples. This resulted in some hexagonal catalyst pattern; however, these areas occurred in small patches and were relatively rare, perhaps accounting for about 1% of the total sample area. Most of the nanospheres did not dissolve, presumably because they were protected by the layer of gallium.

The molybdenum grid samples fared better when it comes to actually dissolving the spheres. There were large areas where all of the spheres dissolved completely. However, the gallium layer was not quite as thick as the layer on the copper plates, and, as a result, most of the area where the spheres dissolved did not have sufficient gallium to create a hexagonal array of gallium droplets. Nonetheless, there were still areas that were clearly patterned sufficiently to be used to attempt nanowire growth in the MOCVD system.

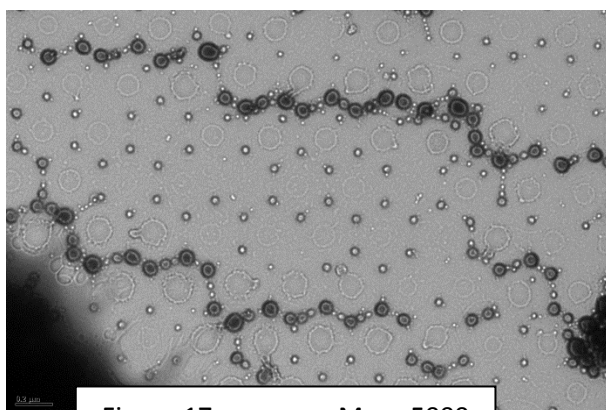


Figure 17: copper – Mag x5000
Hexagonal array of Ga droplets

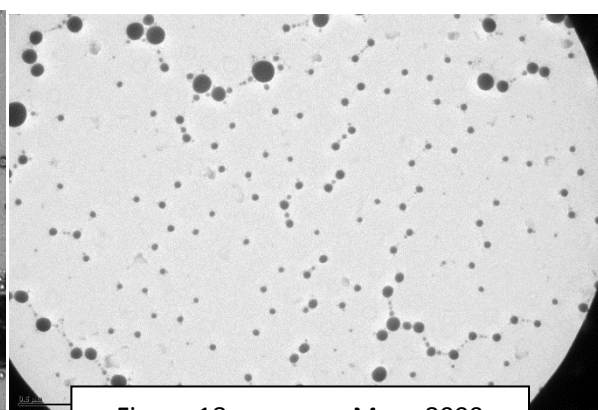


Figure 18: copper – Mag x8000
Hexagonal array of Ga droplets

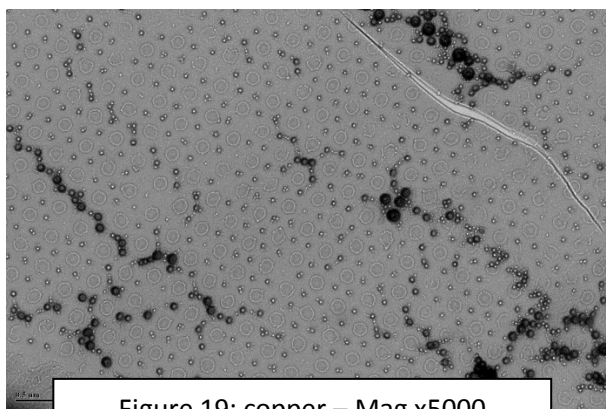


Figure 19: copper – Mag x5000
Hexagonal array of Ga droplets

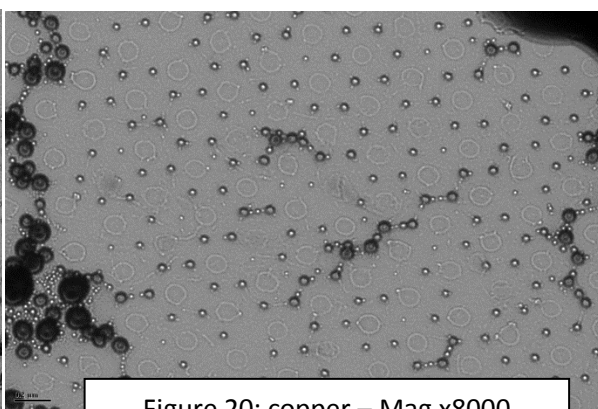


Figure 20: copper – Mag x8000
Hexagonal array of Ga droplets

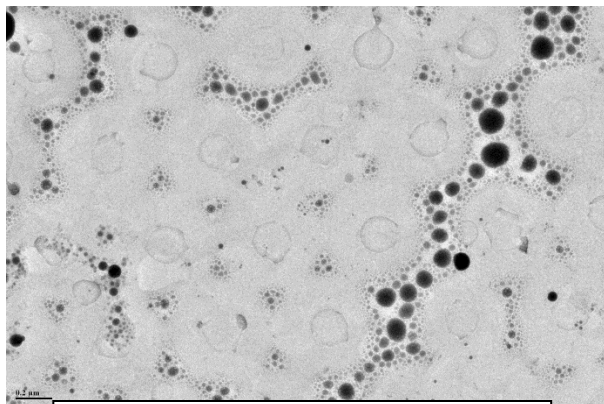


Figure 21: molybdenum – Mag x8000
Hexagonal array of Ga droplet clusters

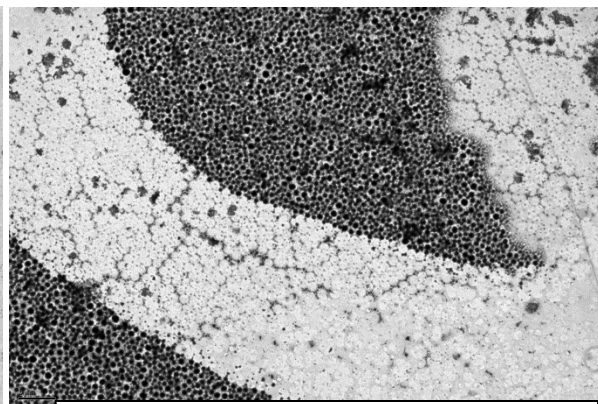


Figure 22: molybdenum – Mag x800
Large region of hexagonal droplet arrays

Nanowire Growth

Initially, there were some problems with the MOCVD system. The Nano-SE Program at SDSM&T had been working on it, and when they put everything back together, the flow rate of the gallium and arsenic wouldn't stabilize, but would instead spike and oscillate erratically. Eventually, this problem was solved by replacing some parts in the machine.

The first growth using the MOCVD system yielded definite growth of large chunks of gallium arsenide, as confirmed by the EDX (Energy Dispersive X-Ray Spectroscopy) element detector in the TEM. However, there was no visible indication of nanowire growth, indicating that to actually grow nanowires requires a more precise control of growth conditions than we were anticipating. The conditions used in the MOCVD system were as follows: the sample was heated to 575 °C, and gallium and arsenic were flowed into the chamber for 10 minutes. Arsenic was initially flowed into the chamber to saturate it, and the flow rate for arsenic was kept much higher than gallium, so that the V/III ratio was around 100:1. Both gallium and arsenic were carried in by other elements in gas form (Trimethylgallium and Arsine). In this growth and in all

subsequent growths, pressure was kept at a constant 20 Torr and there was a constant flow of hydrogen at the rate of 0.7 liters/minute.

The second growth using the MOCVD system yielded a surprising amount of very long and thin nanowires. The growth conditions were changed as follows: the sample was heated to 550 °C, and TMGa and Arsine were then flowed into the chamber at the same time, with flow rates so that the V/III ratio was 4:1. TMGa had a flow rate of 6 SCCM diluted to 6% and AsH₃ had a flow rate of 0.5 SCCM. They were flowed for 10 minutes. There was no pre-saturation of the chamber with either trimethylgallium or arsine. However, a machine malfunction interrupted the arsine flow, so that at some point during the ten minutes it dropped to virtually zero. Despite this, the results were examined for nanowire growth.

On the third growth of the MOCVD system, arsine was accidentally flowed into the chamber prior to the growth phase due to an operator error. Everything else was kept the same, except the growth phase was reduced to 5 minutes. There was no interruption in arsine flow due to a machine malfunction.

For fourth growth, instead of using the vacuum evaporator to achieve a thin layer of gallium, gallium was flowed for 20 seconds before the growth phase, hopefully replicating the vacuum evaporation process in the MOCVD system. When the gallium was flowed, conditions were the same as the conditions used during the actual growth process. Then, a growth phase was run with a 4:1 V/III ratio for 5 minutes at 550 °C and 20 Torr. However, the flow rates were reduced by a factor of 2, to 3 SCCM of TMGa and 0.25 SCCM of AsH₃.

For growths 5 and 6, vacuum evaporation was again used to form gallium droplets. However, for both growths the substrate was not a copper or molybdenum grid, but a gallium arsenide substrate. In both cases, there was no pre-saturation with either of the growth gases.

Growth temperature was 550 °C. Growth length was 5 minutes. TMGa was flowed at 6 SCCM diluted to 6%. In growth 5, arsine was flowed at 0.32 SCCM; in growth 6, arsine was flowed at 0.20 SCCM. The results of these two growths were indiscernible.

For growth 7, the growth procedure was changed up. The surface was still a gallium arsenide substrate. Growth temperature was 600°C. Hydrogen flow rate was changed to 0.35 L/min. TMGa was flowed at 3.0 SCCM, and arsine was flowed at 0.12 SCCM. Growth length was 5 minutes. Instead of vacuum evaporation, a pre-saturation was used with gallium to form Gallium droplets before the growth process. This occurred at growth temperature. Gallium was flowed at 5.0 SCCM for 20 seconds, and growth began immediately afterwards. During the process of heating the chamber, arsine was flowed at 3 SCCM. It was turned off just as the gallium pre-saturation began.

For growth 8, arsine was again during the heating up process, and gallium was flowed at 5.0 SCCM for 20 seconds for pre-saturation. However, the growth temperature was changed to 450°C. TMGa was flowed at 3.0 SCCM, and arsine was flowed at 3.0 SCCM. Growth length was 5 minutes. Everything else was the same as in growth 7.

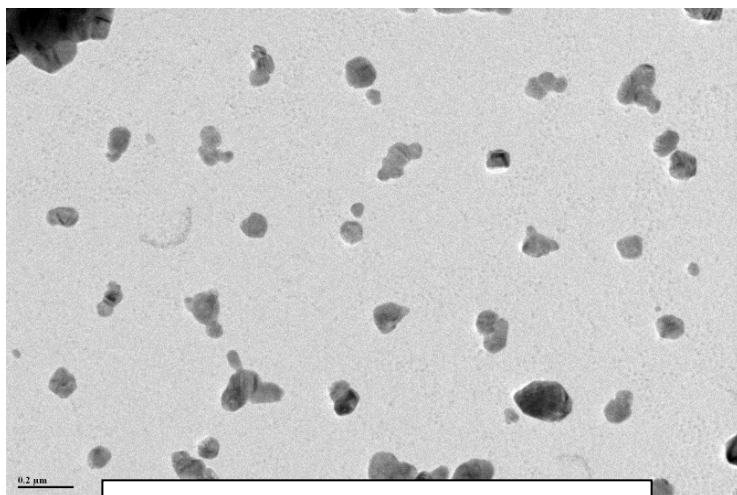


Figure 23: Growth 1: TEM – Mag x10k
Hexagonally arranged GaAs chunks

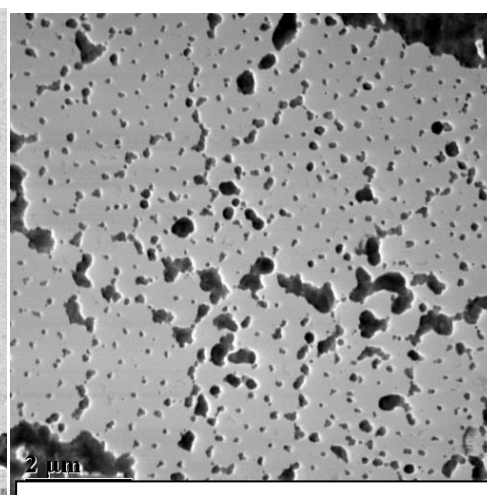


Figure 24: Growth 1: SEM – Mag x40k
SEM: GaAs chunks

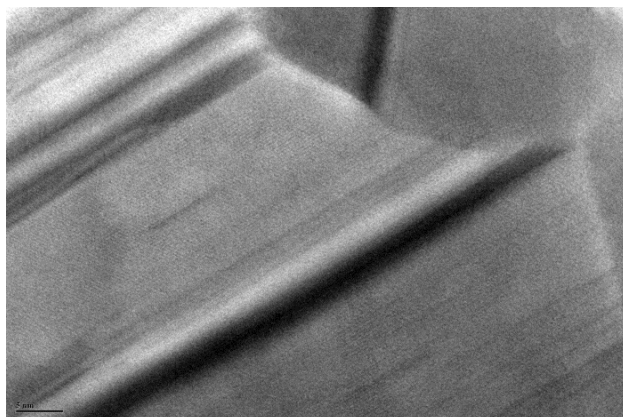


Figure 25: Growth 1: TEM – Mag x400k
Close up of GaAs chunk reveals crystal structure

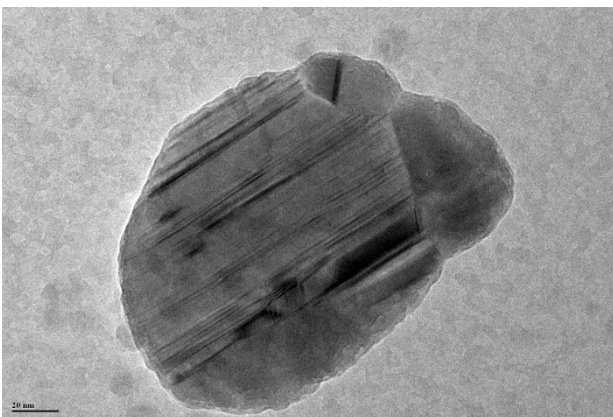


Figure 26: Growth 1: TEM – Mag x100k
GaAs chunk

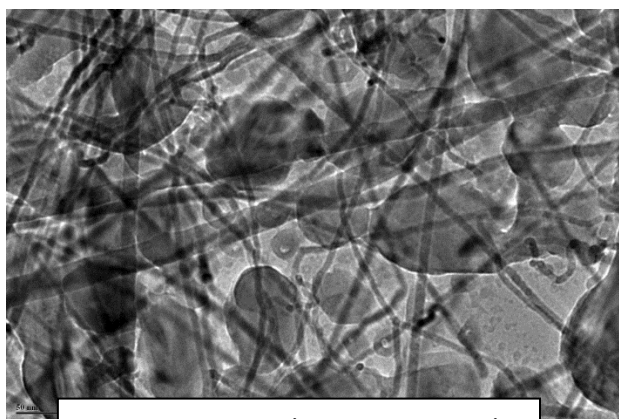


Figure 27: Growth 2: TEM Mag 50k
Nanowires

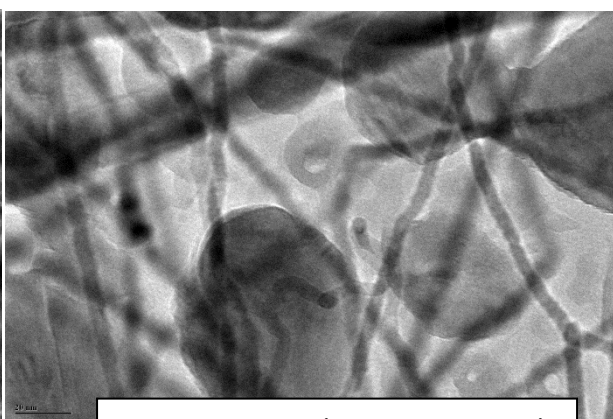


Figure 28: Growth 2: Tem Mag 120k
Nanowires: difficult to focus

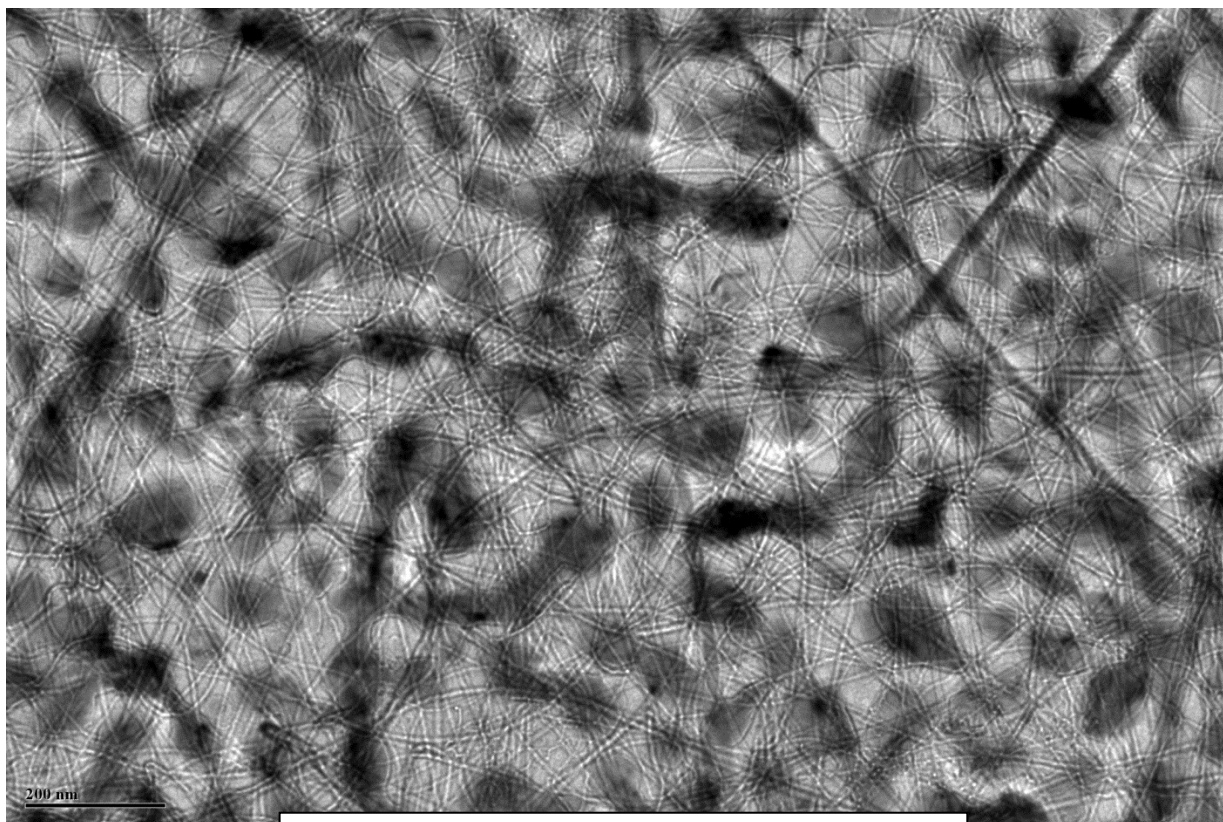


Figure 29: Growth 2: TEM Mag 15k
Long, narrow nanowires

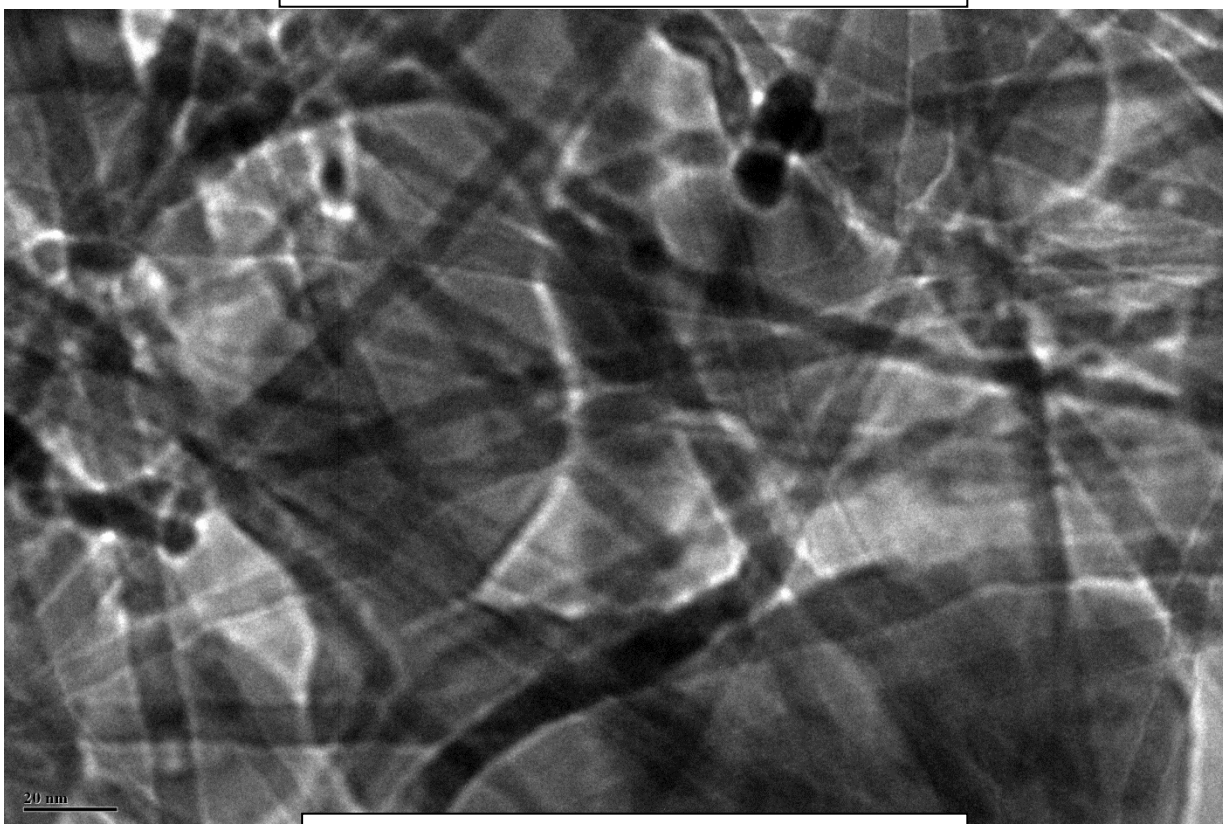


Figure 30: Growth 2: TEM Mag 100k
Many interwoven nanowires

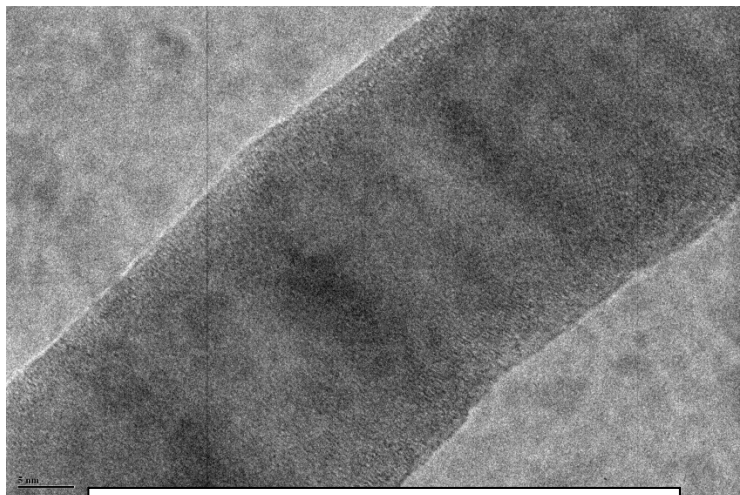


Figure 31: Growth 3: TEM Mag 400k
Close up of nanowire

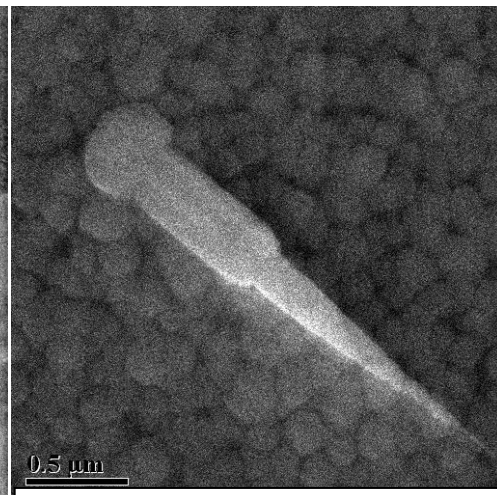


Figure 32: Growth 3: SEM Mag 150k
SEM image of "tadpole" nanorod

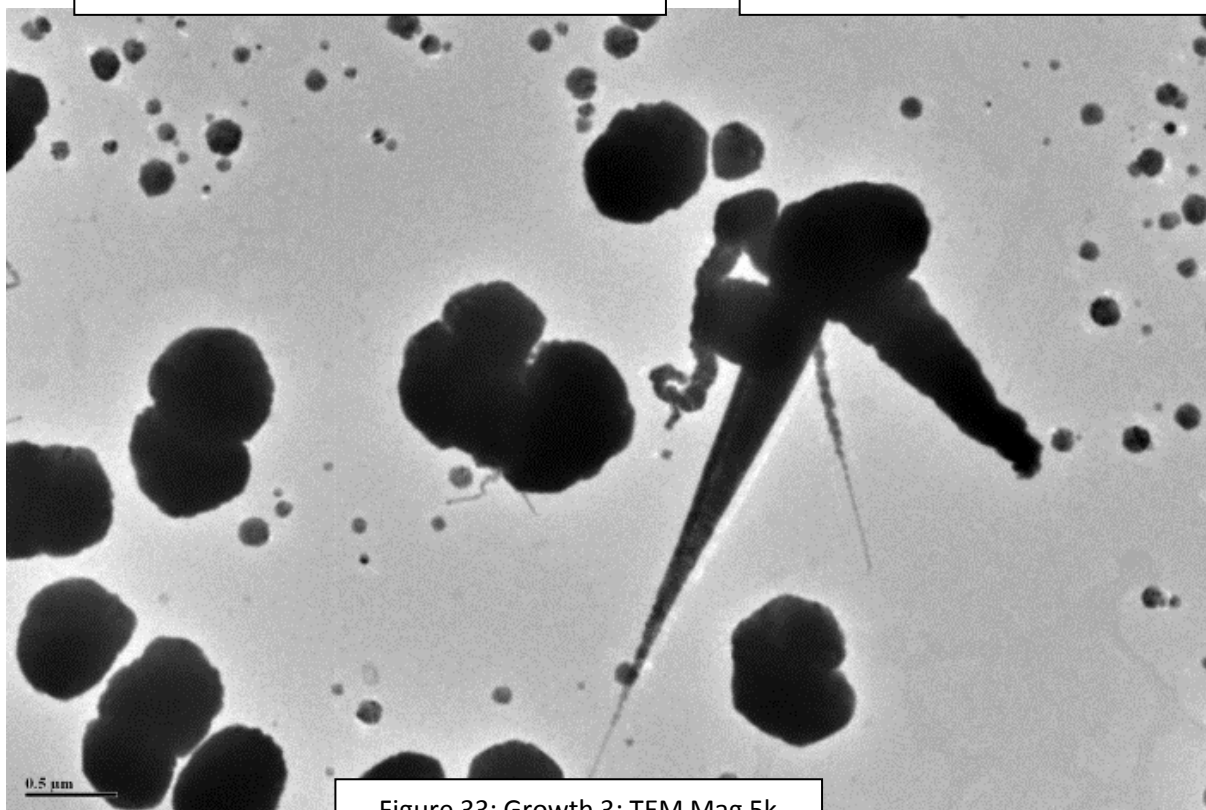


Figure 33: Growth 3: TEM Mag 5k
Large nanorods tapering to
nanowires

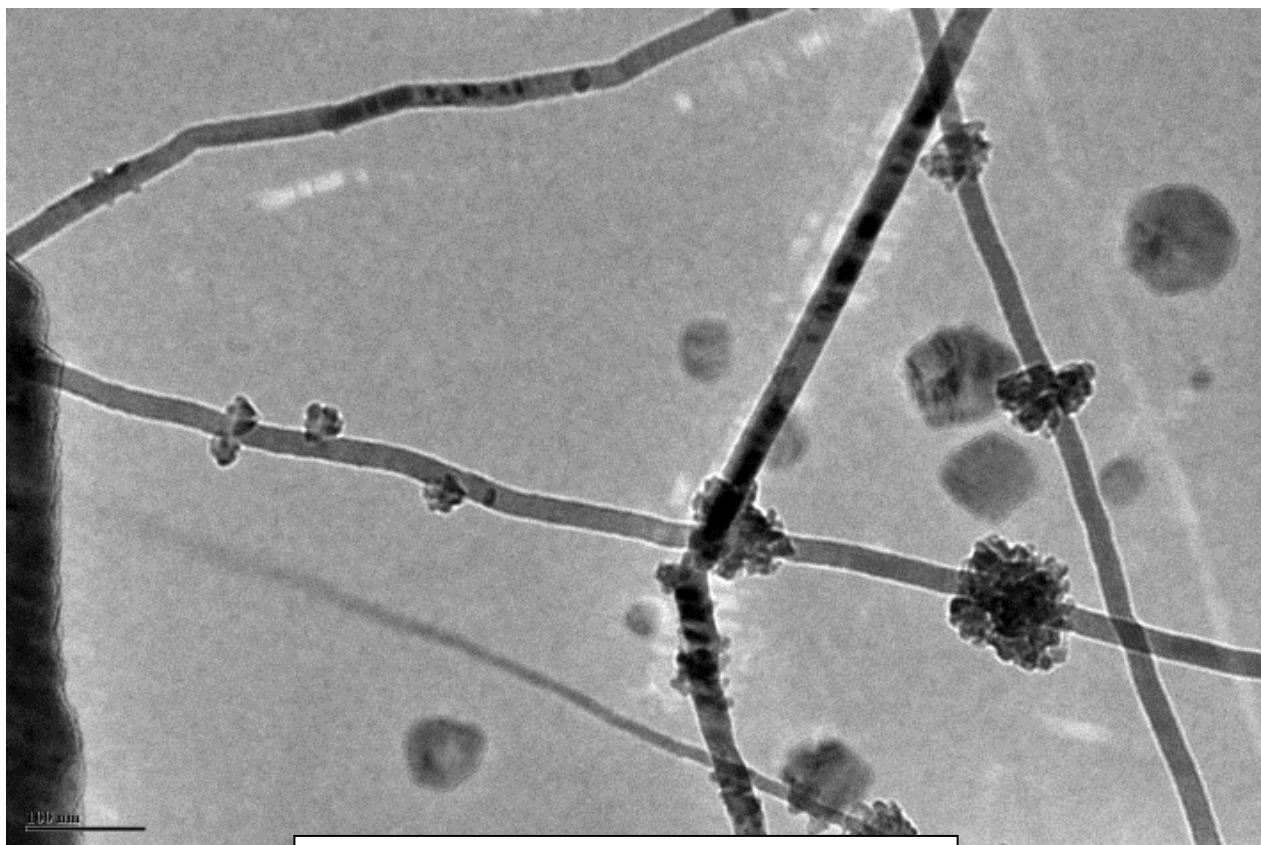


Figure 34: Growth 3: TEM Mag 25k
Nanowires accompanying the nanorods

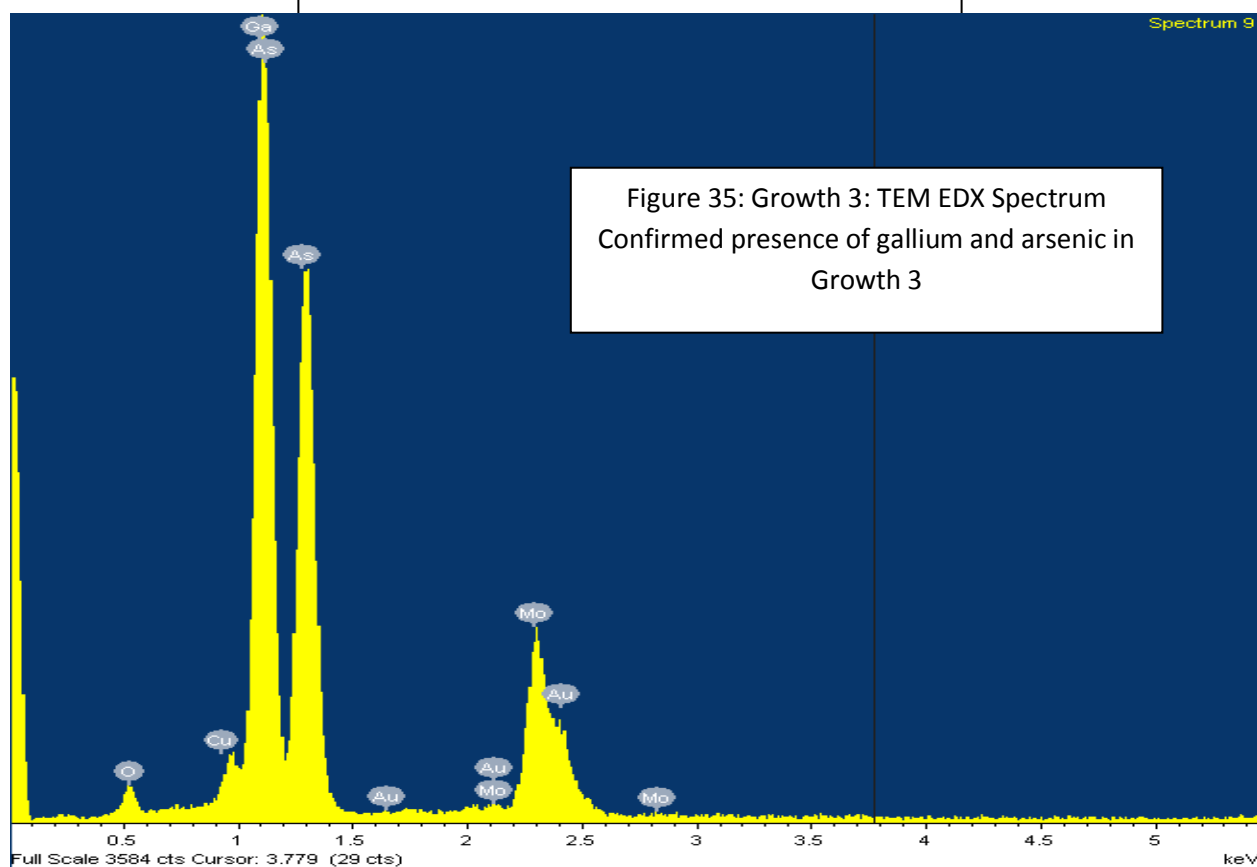


Figure 35: Growth 3: TEM EDX Spectrum
Confirmed presence of gallium and arsenic in
Growth 3

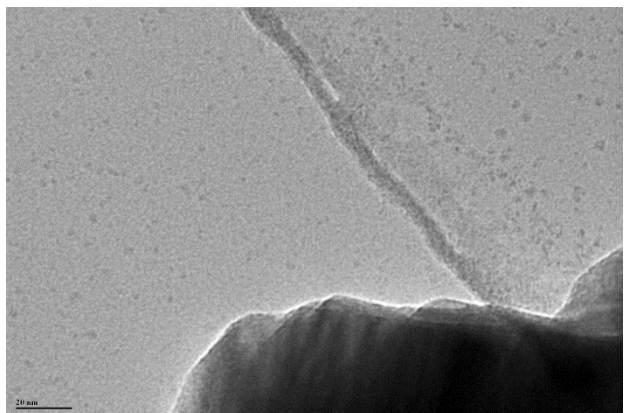


Figure 36: Growth 4: TEM Mag 120k
Possible nanowire – possible surface boundary

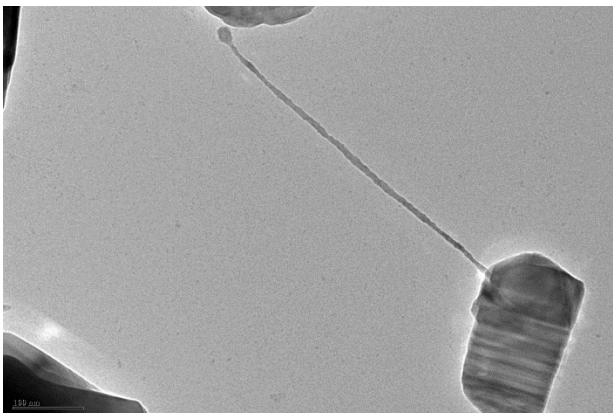


Figure 37: Growth 4: TEM Mag 30k
Likely nanowire from GaAs chunk

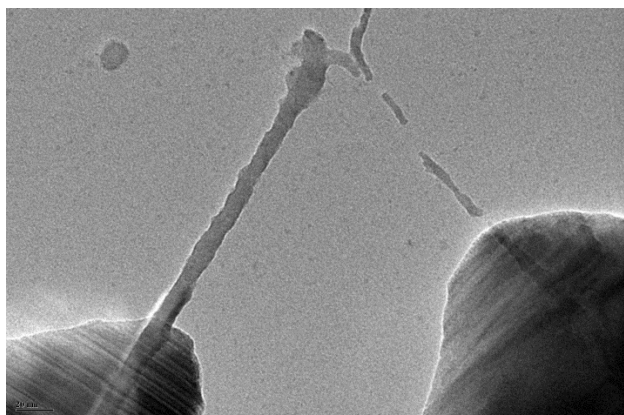


Figure 38: Growth 4: TEM Mag 40k
Likely nanowire from GaAs chunk

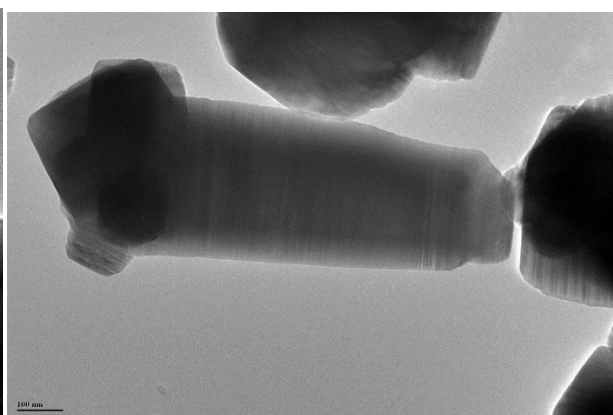


Figure 39: Growth 4: TEM Mag 20k
Large GaAs crystal – nanorod-like

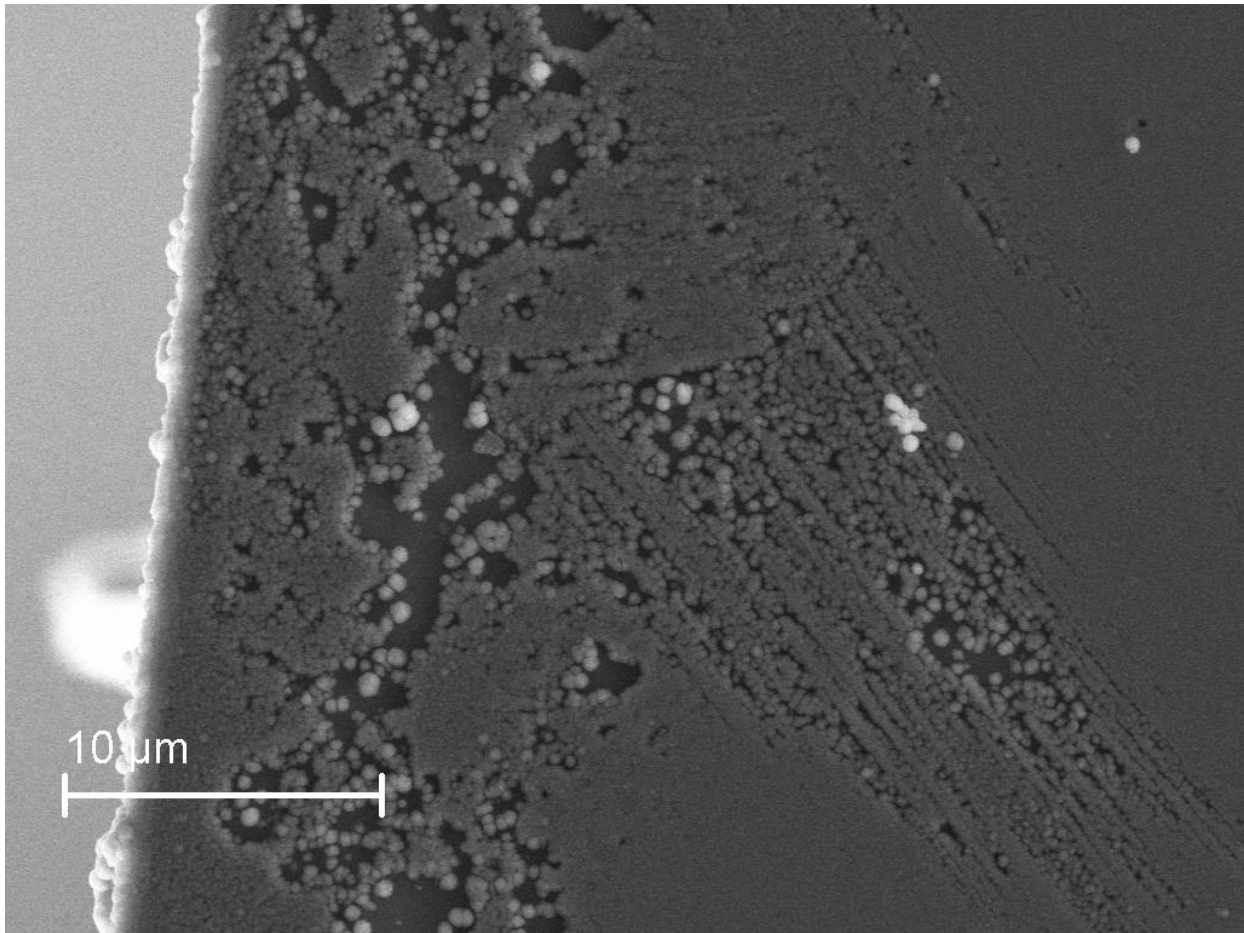


Figure 40: Growth 6: SEM Mag 7k
Large GaAs crystals on a GaAs substrate

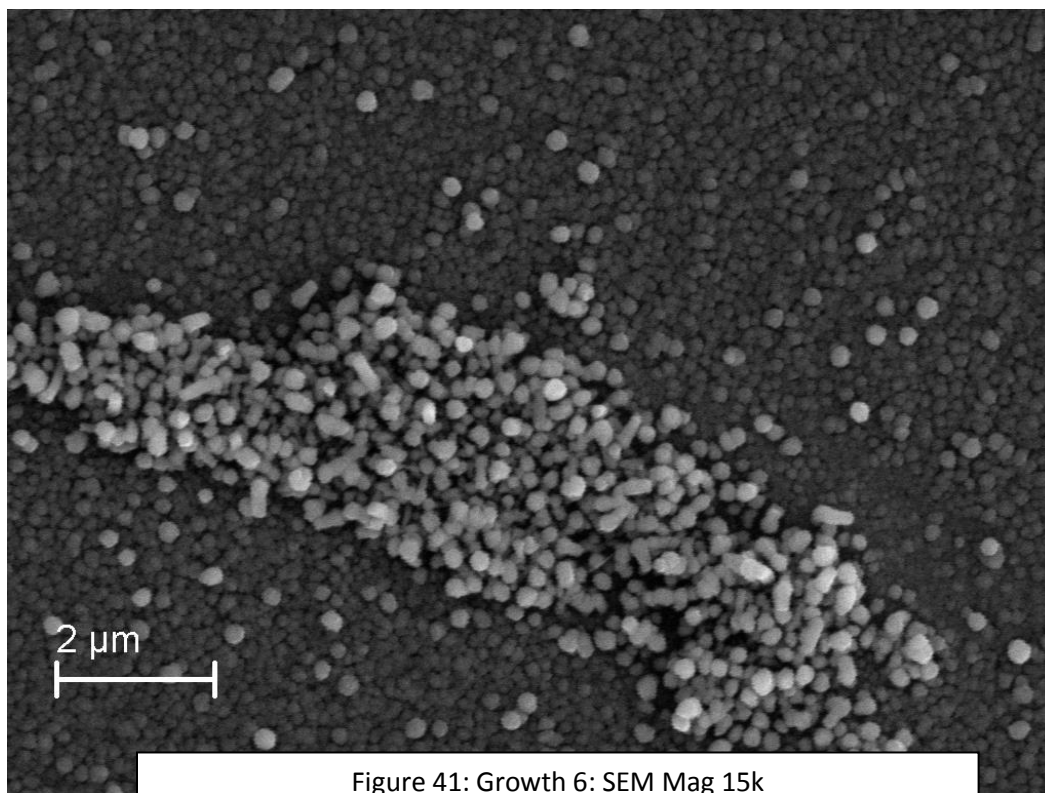


Figure 41: Growth 6: SEM Mag 15k
GaAs Crystals – slight nanorod appearance – on a GaAs substrate

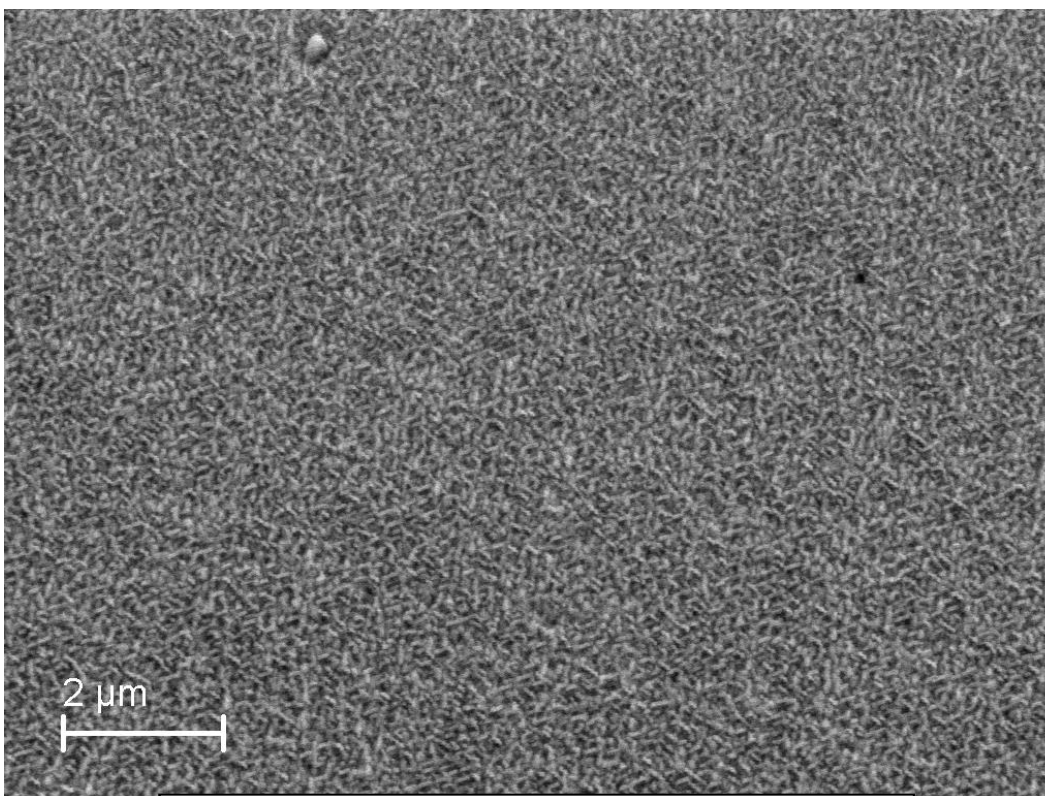


Figure 42: Growth 7: SEM Mag 21k
Possible short nanowires on GaAs substrate

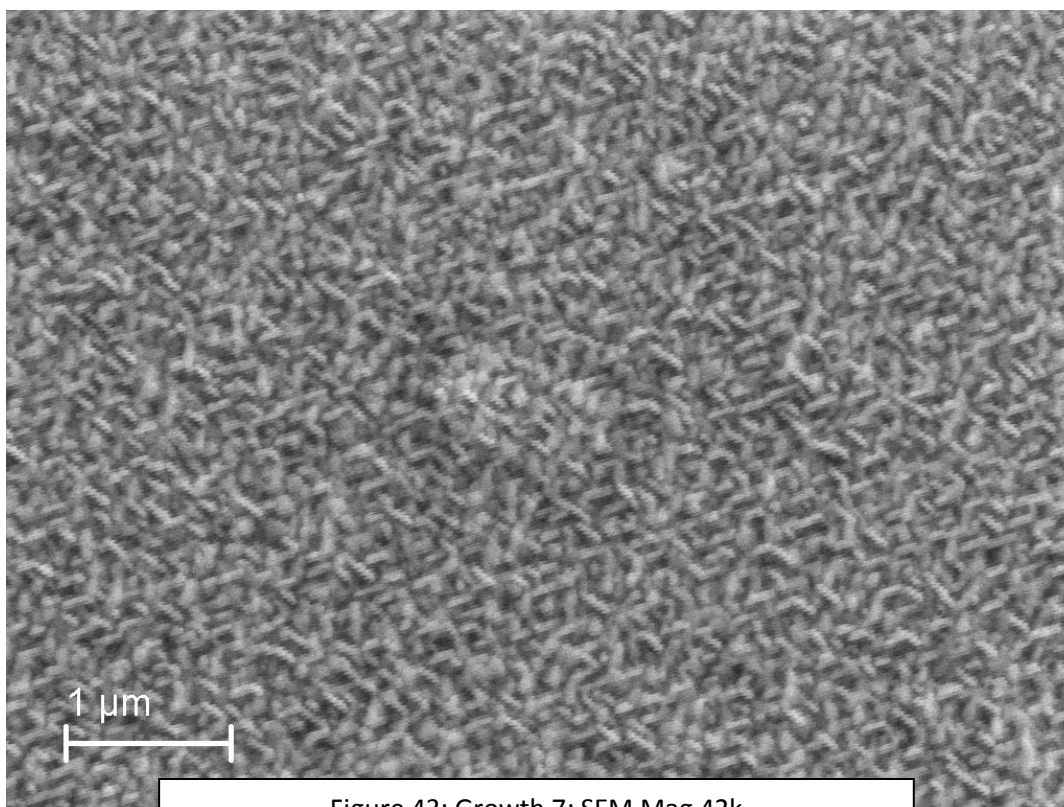


Figure 43: Growth 7: SEM Mag 42k
Possible short nanowires on GaAs substrate

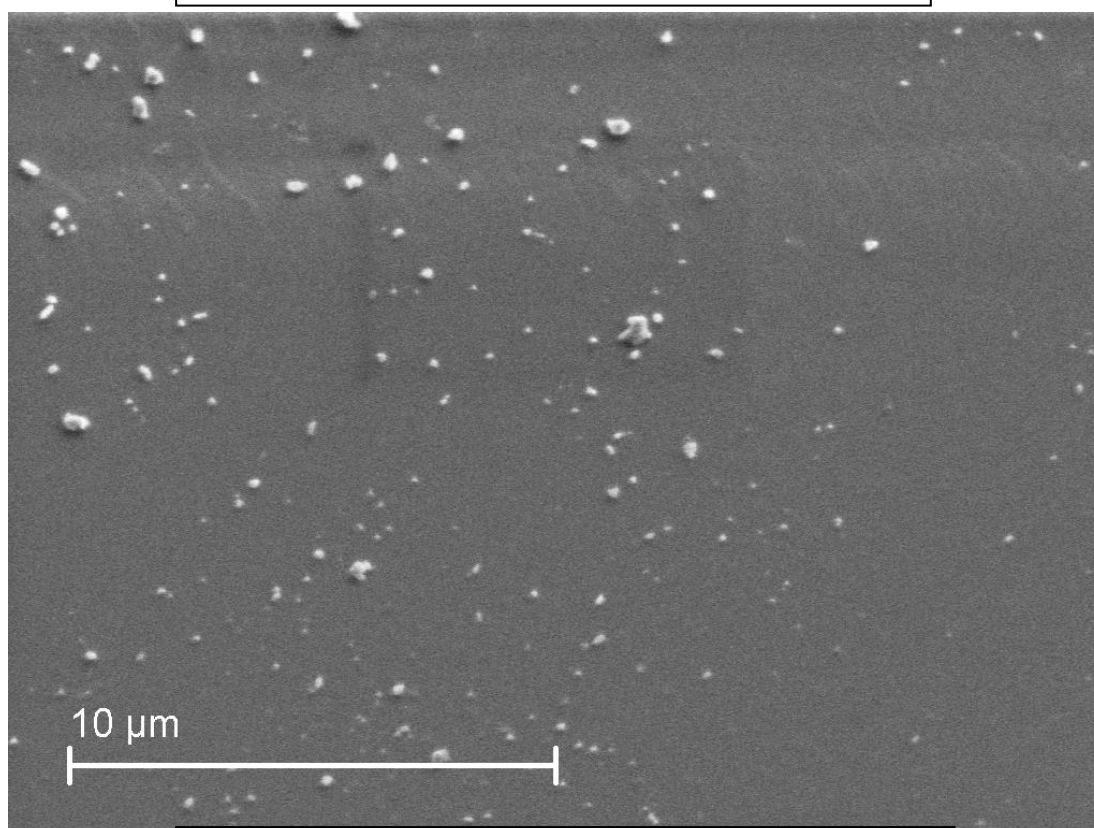


Figure 44: Growth 8: SEM Mag 12k
Large GaAs crystals, no nanowires, on GaAs substrate

Discussion

We successfully completed nanosphere lithography with polystyrene nanospheres of different sizes, ranging from 356 to 540nm. From there, we successfully used vacuum evaporation to evaporate gallium, the catalyst to be used in the MOCVD process, onto the nanospheres to create a layer and deposit gallium in the spaces between the spheres. We also successfully demonstrated the ability to dissolve the spheres, leaving only the gallium that was in the spaces between the spheres behind.

On our first growth, gallium arsenide chunks were observed arranged in a hexagonal pattern created by the nanospheres. There was no visible sign of nanowires or nanowire-like objects. The chunks, upon closer inspection, appeared to have a crystal-like structure, another indication of their composition of gallium arsenide.

When nanowire growth was observed for the first time (growth 2), it was unclear what the nanowires were actually made of. The EDX element detector picked up lots of gallium and oxygen, but there was only the slightest indication of arsenic. This could be due to the tendency of the larger gallium droplets deposited through vacuum evaporation to simply grow larger and not to form anything resembling a nanowire, which resulted in large “chunks” of what seemed to be pure gallium on the carbon film. Nonetheless, there were clearly many nanowires of impressive narrowness and extreme length. Most were around 5nm in diameter, with lengths reaching several micrometers, giving them a length/width ratio of around 1000:1. They were also very randomly directed, with some staying almost parallel to the carbon film, some sticking out almost vertically, and some in all directions in-between. This made it difficult to focus and get a

clear image of a small section of the substrate. The results of this growth indicated that to achieve GaAs nanowires using a Ga catalyst, a low V/III ratio is required.

For the third growth of the MOCVD system, we accidentally flowed some arsine into the chamber prior to the growth phase due to an operator error. Despite this, the growth process was continued, since the results would likely be interesting. What was discovered was far different from the first and second runs of the MOCVD system. As can be seen in the pictures of growth 3, there were large “nanorods,” ranging from around 50 to several hundred nanometers in diameter. Additionally, many were cone-shaped, tapering from an initial diameter of several hundred nanometers down to the extremely narrow width of 5nm that was found in the previous growth. Our initial explanations could not fully explain this effect; it’s possible that either the gallium droplet shrank, resulting in the gradual tapering of the nanorod, or the droplet grew, resulting in the widening of a nanowire.

Despite the presence of these large rod and cone structures, some patches were found of nanowires that resembled that of the previous test (growth 2). Taking an extremely magnified image, small bands were found perpendicular to the growth direction of the nanowire, indicating a composition of gallium arsenide (as opposed to just gallium or gallium oxide or any other possibility given the growth conditions): See Figure 31: Growth 3: TEM Mag 400k. Additionally, using the EDX element detector, the presence of both gallium and arsenic was confirmed, indicating the composition of the nanorods to be gallium arsenide.

For the fourth growth, the growth process was changed as follows: rather than using the vacuum evaporator to create an initial layer of gallium, gallium was flowed into the vacuum chamber for 20 seconds prior to the growth phase. However, the results that this process yielded were less than exciting compared to the previous two tests. Large gallium arsenide (as confirmed

by EDX) chunks were present, and nanowires were extremely difficult to find. Nonetheless, some nanowires were clearly visible, seemingly growing out of large chunks of gallium arsenide, or vice versa. We are unsure why they grew in this manner.

Growths 5 and 6 yielded extremely similar results, which is somewhat expected since the only difference between them was 0.12 SCCM of arsine during the growth process. We had significant trouble focusing the SEM at a high magnification, but from what we could see, it was mostly uninteresting. Perhaps there was too much gallium deposited during the vacuum evaporation. The only observed, which completely covered both substrates, was large chunks that didn't appear especially crystallized. On Growth 6, we did see some slight indications of nanowires starting to grow; however, with the images taken, it was inconclusive. See figure 41.

Growth 7 had some interesting results. It appears as if there is a dense sheet of thicker, short, stubby nanowires, 25 to 50nm in diameter and perhaps several hundred nanometers in length. We were experiencing some difficulties getting the SEM to focus at a magnification high enough to get a closer look than can be seen in the images taken. Like growth 2, these results seem to indicate that the key to growing nanowires is a low V/III ratio, which was only 1.8 in this growth.

Growth 8 was far less interesting. Nothing was found to focus on at high magnifications, indicating that there actually was not anything there to see. What was seen was very large (presumably gallium arsenide) chunks spaced about 1 to 5 micrometers apart. This was fairly uniform across the whole substrate. For growths 5 through 8, it is possible that the same things were not observed because they were examined using a different piece of equipment (SEM vs. TEM). However, this is somewhat unavoidable, since the TEM cannot be used on a solid gallium

arsenide substrate. Additionally, a fairly high resolution on the SEM was achieved, so we have confidence that if there was something significant to see, we would have seen it.

Conclusion

In this study, we attempted to grow gallium arsenide nanowires using MOCVD for the potential use in photovoltaic cells. While it was definitively found that nanowires of extreme length and small width can be grown using the processes outlined in this paper, it was also extremely difficult to reproduce the exact growth conditions that yielded this (since the growth we saw resulted from a machine error), and the composition materials of the nanowires could not be accurately identified, which means the composition of the nanowires may or may not have been gallium arsenide. More growths should be done to establish the exact growth conditions that results in the long and narrow nanowires that we were hoping to find.

While nanosphere lithography and vacuum evaporation of a catalyst onto these nanospheres was successfully achieved and the nanospheres were successfully dissolved to leave only a hexagonal array of catalyst droplets, no nanowires were actually grown out of a substrate like this due to time constraints. Given that nanowires have been grown out of catalyst droplets haphazardly arranged, it seems likely that nanowires could be grown out of catalyst droplets that are arranged orderly. Additional tests would need to be done to confirm this.

The composition of the nanorods, which were far thicker than the nanowires we were trying to grow, was confirmed. While their composition was what we were hoping for – gallium arsenide – their morphology as rods was not. However, in the same sample where confirmed gallium arsenide rods were found were also a few scattered nanowires and it seems likely that their composition would be the same, since the rods generally tapered to nanowires before

terminating. Again, however, the exact composition of these wires was not confirmed. Additional tests would be necessary to confirm the composition of nanowires grown.

The growths on GaAs (111)B substrates were, for the most part, unproductive in terms of nanowire growth. Despite this, on one sample the possibility of short, stubby nanowires was observed. However, we failed to achieve sufficiently high resolution to be absolutely sure of this. One thing that the results have indicated is that, when using Ga as a catalyst, a low V/III ratio is highly recommended, as it has yielded nanowires or nanowire like objects far more consistently than growths with a higher V/III ratio.

Recommendations for additional future work are to continue to attempt to grow nanowires on (111) substrates made out of elements like gallium arsenide to create vertically aligned nanowires. Additional tests should be done to discover exactly what growth conditions will yield nanowires most consistently, both on copper or molybdenum grids and on gallium arsenide substrates. Perhaps a direct comparison of vacuum evaporation and MOCVD gallium pre-saturation should be done to test the different impacts that these two catalyst arrangement techniques have on nanowire growth. Additional testing should also be done to confirm the composition of any nanowires that are successfully grown. Finally, nanosphere lithography should be explored in greater depth to attempt to achieve hexagonally arranged mono/double layers far more consistently than we were able to in this study.

References

1. Cirilin, G. E., Bouravleuv, A. D., Soshnikov, I. P., Samsonenko, Y. B., Dubrovskii, V. G., Arakcheeva, E. M., Tanklevskaya, E. M., & Werner, P. (2010). Photovoltaic properties of p-doped gas nanowire arrays grown on n-type gas(111)b substrate. *Nanoscale Research Letters*, 5(2), 360-363. Retrieved from <http://www.nanoscalereslett.com/content/5/2/360>
2. Tian, B., Kempa, T. J., & Lieber, C. M. (2009). Single nanowire photovoltaics. *Chemical Society Reviews*, 38(1), 16-24. Retrieved from <http://pubs.rsc.org/en/content/articlepdf/2009/cs/b718703n>
3. Mohan, P., Bag, R., Slingh, S., Kumar, A., & Tyagi, R. (2011). Mechanism of self assembled growth of ordered gas nanowire arrays by metalorganic vapor phase epitaxy on gas vicinal substrates. *Nanotechnology*, 23(2), 1-5. Retrieved from http://iopscience.iop.org/0957-4484/23/2/025601/pdf/0957-4484_23_2_025601.pdf
4. Bjork, M. T., Ohlsson, B. J., Sass, T., Persson, A. I., Thelander, C., Magnusson, M. H., Deppert, K., Samuelson L., & Wallenberg, L. R. (2002). One-dimensional heterostructures in semiconductor nanowhiskers. *Applied Physics Letters*, 80(6), 1058. doi: 10.1063/1.1447312
5. Noborisaka, J., Motohisa, J., Hara, S., & Fukui, T. (2005). Fabrication and characterization of freestanding gas/algaas core-shell nanowires and algaas nanotubes by using selective-area metalorganic vapor phase epitaxy. *Applied Physics Letters*, 87(1), doi: 10.1063/1.2035332
6. Banerjee, R., Bhattacharya, A., Genc, A., & Arora, B. M. (2006). Structure of twins in gas nanowires grown by the vapour-liquid-solid process. *Philosophical Magazine Letters*, 86(12), 807-816. Retrieved from <http://web.ebscohost.com/ehost/pdfviewer/pdfviewer?sid=459852fa-789f-4a49-81c8-e30bd6bf3c8b@sessionmgr11&vid=11&hid=9>
7. Guo, Y. N., Zou, J., Paladuga, M., Wang, H., Gao, Q., Tan, H. H., & Jagadish, C. (2006). Structural characteristics of gasb/gas nanowire heterostructures grown by metal-organic chemical vapor deposition. *Applied Physics Letters*, 89(1), Retrieved from <http://web.ebscohost.com/ehost/detail?vid=5&sid=c8824b10-44f8-4ba4-8214-526e0f7c06af@sessionmgr10&hid=11&bdata=JnNpdGU9ZWhvc3QtbGl2ZQ==>
8. Czaban, J. A., Thompson, D. A., & LaPierre, R. R. (2009). Gas core-shell nanowires for photovoltaic applications. *Nano Letters*, (1), 148-154. Retrieved from <http://pubs.acs.org/doi/pdf/10.1021/nl802700u>
9. Knier, G. (2002). *How do photovoltaics work?*. Retrieved from <http://science1.nasa.gov/science-news/science-at-nasa/2002/solarcells/>

10. *Photovoltaic cell conversion efficiency*. (2013, April 22). Retrieved from http://www.eere.energy.gov/basics/renewable_energy/pv_cell_conversion_efficiency.html
11. MacKay, D. J. (2009). *Sustainable energy without the hot air*. (pp. 38-49). UIT. Retrieved from http://www.inference.phy.cam.ac.uk/withouthotair/c6/page_38.shtml
12. Mohammad, S. N. (2008). Analysis of vapor-liquid-solid mechanism for nanowire growth and a model for this mechanism. *Nano Letters*, 8(5), 1532-1538. Retrieved from <http://pubs.acs.org/doi/abs/10.1021/nl072974w>
13. Breuer, S., Karouta, F., Tan, H. H., & Jagadish, C. (2012). MOCVD growth of GaAs nanowires using Ga droplets. *Conference on Optoelectronic and Microelectronic Materials and Devices, Proceedings, COMMAD*, 39-40. doi: 10.1109/COMMAD.2012.6472349

Acknowledgments

The funding for this research came from the National Science Foundation. Thanks for their support via the NSF REU Back to the Future Award DMR-1157074. Thanks to advisors Dr. Phil Ahrenkiel and REU site director Dr. Michael West for their direction and guidance, Professor of English Dr. Alfred Boysen for his aid and critique in writing and speaking. Additionally, I would like to offer special thanks Srujan Mishra, Nan Zheng, and Jon Fisher for all of their help and assistance. Finally, thanks to all of the faculty and staff at SDSM&T and the other REU students for their help.