Gallium Nitride (GaN) Quantum Dot Layer Formation

by

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INTRODUCTION

Gallium nitride (GaN) is a III-V semiconductor material commonly used for optoelectronic applications because of its properties in the short wavelength range (350 nm) with a wide-band gap value of 3.39 eV at room temperature. It is also used in high-temperature, high-power, and high-frequency electronic devices. Examples include light-emitting diodes (LEDs) [1], blue and ultraviolet lasers, and solar cells.

GaN exists in two forms: the hexagonal wurtzite structure and the cubic zinc-blende structure. The hexagonal wurtzite is stable and can be grown on sapphire, SiC, and Si substrates. The cubic zinc-blende structure is metastable, but can be stabilized by the choice of substrate or growth conditions. Advantages of the zinc-blende structure include the production of laser cavities and the ease of doping. It also has the potential for a higher saturated electron drift velocity and lower band gap than wurtzite GaN [2].

Despite prevalent technological applications of GaN, its properties still need to be understood and can be improved. Amorphous (a-GaN), microcrystalline (μc-GaN), and polycrystalline (pc-GaN) gallium nitride films can be produced more cheaply than crystalline GaN [3]. Because the growth of GaN is rather expensive, new synthesis methods are being explored. In the Belcher group, monodisperse, crystalline GaN quantum dots (QDs) in the 3 to 5 nm diameter range are synthesized using precursors like gallium chloride, triethyl amine, chloroform, and trioctylphosphine oxide (TOPO). Commercial GaN powder, however, comes in different sizes, agglomerates, and is not necessarily crystalline. Heretofore, these quantum dots will be referred to as Jifa GaN.

At such small scales, quantum confinement will affect the optical and electronic properties of GaN [4]. The energy gap increases in nanoparticles and there is an optical shift

towards short wavelength regions [5]. In a sufficiently small semiconductor, or quantum dot, there are discrete values for the density of states. This discrete energy spectrum of conduction electrons results in unique optical and electronic properties that differ from those found in bulk semiconductor materials. For example, if an electron-hole pair (exciton) is formed inside a nanoparticle whose diameter is equal to or smaller than the natural electron-hole separation, the number of degrees of freedom for the exciton is zero and therefore no motion is possible [6].

The goal of this work is to deposit uniform monolayers of these GaN quantum dots so that electronic properties can be measured. With improved understanding of GaN quantum dot properties, in the future, one will be able to construct devices. Several methods of layer formation were explored, including layer-by-layer modification, spin-coating, drop-casting, and using viral templates obtained from biopanning results.

Research Goals

This work focused on methods by which monolayers of GaN QDs could be deposited in a controlled and repeatable fashion. Because the GaN QDs are believed to have quantum confinement, their electronic properties may differ from bulk GaN and should be measured. To accomplish this goal, GaN QDs need to be made into layers of controlled thickness and packing. Several methods are explored in this research, including layer-by-layer modification, spin-coating, dropcasting, and viral templates.

MATERIALS AND METHODS

Surface Ligand Exchange of CdSe/ZnS-TOPO Quantum Dots (QDs)

Use 100 μL of stock Evident Technologies CdSe/ZnS quantum dots, which are covered in trioctylphosphine oxide (TOPO) and suspended in toluene. Precipitate QDs in 1 mL ethanol

(EtOH). Centrifuge for 3 minutes at 14,000 rpm. Discard supernatant and resuspend QDs in 1 mL chloroform ($CHCl_3$). Transfer solution to glass vial and add 1 mL mercaptoacetic acid (MAA). Prepare 4 eppendorf tubes with 1 mL ethanol and aliquot 500 μL of QD solution to each tube. Centrifuge for 3 minutes at 14,000 rpm. Discard supernatant and reconstitute in 250 μL 50mM pH9 Tris buffer. Combine in glass vial to form 1 mL of QD solution.

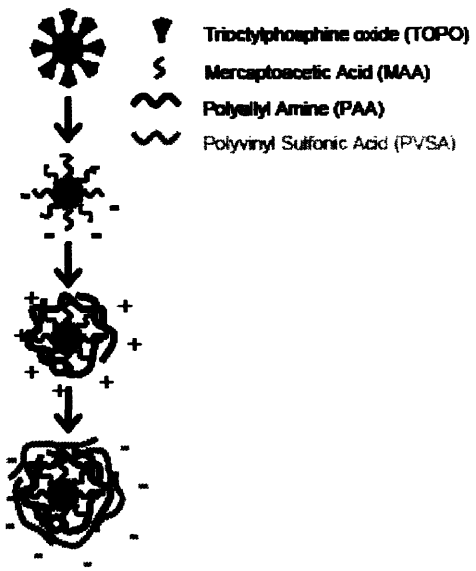


Figure 1. Surface Ligand Exchange of CdSe/ZnS-TOPO Quantum Dots (QDs) [7]. Evident Technologies CdSe/ZnS QDs are denoted in green with a surrounding layer of trioctylphosphine oxide (TOPO) and suspended in toluene. A solvent exchange is first completed whereby toluene is replace by ethanol and then chloroform. In chloroform, negatively charged mercaptoacetic acid (MAA) displaces the TOPO and forms a stable bond. To form other charged nanoparticles for use in electrostatic layer-by-layer deposition, positively charged polyallyl amine (PAA) can be coated around the MAA.

By adding polyallyl amine (PAA) to the QDs, they become positively charged particles. This process is illustrated in Figure 1. The disulfide linkages in the ZnS/CdSe QDs make them

stable and therefore it is easy for the MAA to displace TOPO. The strong new bond formed between MAA and ZnS may be a covalent bond, but has not been confirmed.

To measure QD concentration, use Wavelength Scan II with visible and ultraviolet lamps turned on.

CdSe/ZnS Layer-by-Layer Modification

Oxygen plasma clean glass slide for 90 seconds. This step makes the surface of the glass hydrophilic. Spin-coat 60 μL negatively charged hyaluronic acid (HA) onto glass. Using a silicon master made from a photolithographic mask, polydimethylsiloxane (PDMS) stamps were made. Place the PDMS stamp on the HA while it is still wet. Allow to dry overnight. On the next day, mark the stamp position on the glass and remove stamp. Wash glass slide in 3 35 mL Millipore water baths for 1 minute each. Dry slide in between each bath. Lay slide down so that it dries, but does not collect dust. Put drops of water on either side of the pattern and place cover slips on top. Drop 60 μL of PAA-covered QDs on pattern and place cover slip over it. Make sure bubbles are removed and let sit for 30 minutes with the cover slip to prevent evaporation. Using optical microscope, image the deposited layers.

GaN Quantum Dots Ligand Exchange

Take GaN quantum dots and put in glass vial with 1 mL chloroform ($CHCl_3$). Sonicate suspension for 15 minutes without heat to break up agglomerated QDs. Add 1 mL of mercaptoacetic acid (MAA). Sonicate for 15 minutes without heat. Prepare 4 microcentrifuge tubes with 1 mL of ethanol (EtOH) each. Allocate 500 μL of suspension to each microcentrifuge tube and spin for 4 minutes at 14,000 rpm. Discard waste and add 250 μL of TBS buffer to see if quantum dots are water-soluble.

Spincoating and Dropcasting

Glass slides are oxygen plasma-cleaned for 45 seconds. Spin-coat 40 μL of GaN-chloroform suspension for 60 seconds at 1000 rpm. Let dry.

Biopanning Using Ph.D.-C7C Constrained M13 Library

Phage display is a technique where a peptide sequence is expressed on the surface of a bacteriophage. The selection process, or panning, involves exposing a library of peptide sequences to a target, washing away unbound phage, and eluting the specifically-bound phage. The eluted phage is then amplified and taken through more rounds to find a consensus sequence.

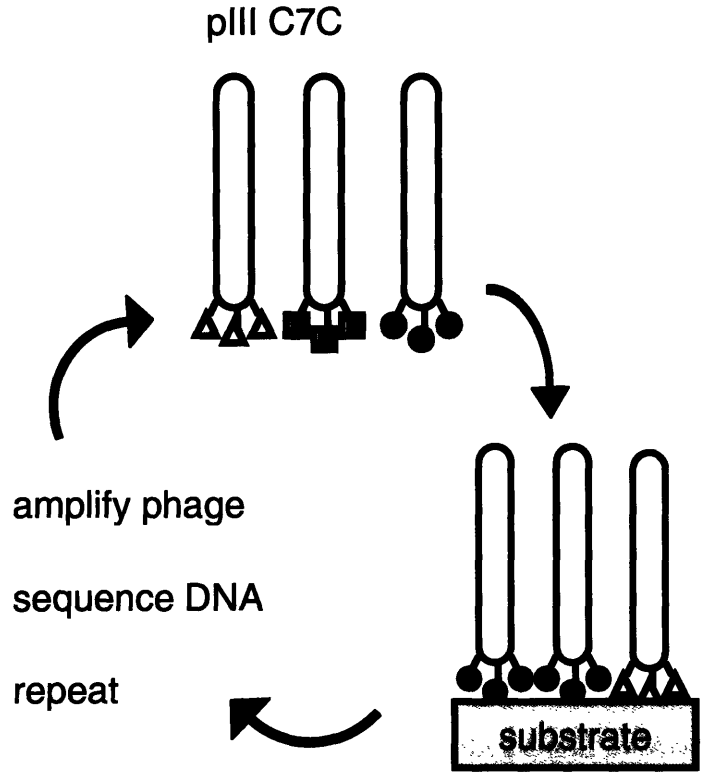


Figure 2. Schematic of Biopanning. Starting with a library of approximately 10^8 phage, each expressing different seven amino acid peptide sequences at the pIII site, which designates the tail end of the phage. A substrate is exposed to the entire library of phage and certain phage will selectively bind to the substrate, which can be amplified and sequenced. This process is repeated

for three to four rounds with harsher conditions each time to reach consensus sequences that specifically bind to the substrate.

The Ph.D.-C7C Phage Display Peptide Library Kit includes random peptide sequences that are seven amino acids long and fused to a coat protein of M13 phage. The sequence is flanked by cysteine residues, which, under non-reducing conditions, will form a disulfide linkage and form cyclized peptides. This library is different from the Ph.D.-7 and Ph.D.-12 libraries, which have linear peptides. Disulfide constrained libraries have been useful in identifying structural epitopes, mirror-image ligands for D-amino acid targets, and leads for peptide-based therapeutics. The library consists of 1.2 x 10^9 sequences compared to a 20^7 = 1.28 x 10^9 possible 7-residue sequences. They are amplified once to yield ~200 copies of each sequence in 10 µl of the phage.

Media and Solutions

- LB Medium:

  Per liter: 10 g Bacto-Tryptone, 5 g yeast extract, 5 g NaCl. Autoclave.

- LB/IPTG/Xgal Plates:

  Mix 1.25 g IPTG (isopropyl beta-D-thiogalactoside) and 1g Xgal (5-Bromo-4-chloro-3-indolyl-beta-D-galactoside) in 25 mL Dimethyl formamide. Solution can be stored at -20 degrees C in the dark. LB medium + 15 g/L agar. Autoclave, cool to <70°C, add 1 mL IPTG/Xgal and pour. Store plates at 4°C in the dark.

- Tetracycline (TET) Stock:

  20 mg/mL in ethanol. Store at -20°C in the dark. Vortex before using.

- TBS:

  50 mM Tris-HCl (pH 7.5), 150 mM NaCl. Autoclave and store at room temperature.

- PEG/NaCl:

  20% (w/v) polyethylene glycol-8000, 2.5 M NaCl. Autoclave, store at room temperature.

- Agarose Top:

  Per liter: 10 g Bacto-Tryptone, 5 g yeast extract, 5 g NaCl, 1 g MgCl2 6H2O, 7 g agarose. Autoclave, dispense into 50 mL aliquots. Store solid at room temperature, melt in microwave as needed.

Start titer culture. Prewash GaN in 1 mL methanol. Sonicate without heat for 3 minutes. Spin down QDs and remove methanol. Repeat 4 times. Add 1 mL 0.2% TBST, vortex, spin down, and remove TBST. Repeat 3 times. Add 10 μL of phage from Ph.D.-C7C library. Rock gently for 60 minutes at room temperature. Discard non-binding phage by pipetting off liquid. Wash substrate 10 times with 1 mL TBST (0.1% for round 1, 0.5% for round 2 and higher), using a new tube every wash. Elute bound phage by adding 450 μL 0.2 mM glycine-HCl (pH 2.2) to substrate and rocking the tube gently for 8 minutes. Immediately pipet liquid to a fresh tube and neutralize with 37 μL Tris-HCl (pH 9.1). Perform titering procedure.

Titering Procedure

Inoculate 10 mL of LB with a single colony of ER2738 bacteria and 10 μL TET and incubate with shaking until mid-log phase (OD 600 is approximately 0.5), which takes about 3 to 4 hours. Place LB/IPTG/Xgal plates in the 37°C incubator at least 2 hours before bacteria culture reaches mid-log. Melt agarose top at least 30 minutes before bacteria reaches mid-log and place 3 mL in tubes in an oven where the temperature is at least 60°C. Label microcentrifuge tubes for the number of phage dilutions that will be performed. In each tube, dispense 100 μL of LB and perform a serial dilution using 10 μL of the phage from the previous tube. When the bacteria is ready, dispense 195 μL of bacteria into a set of microcentrifuge tubes. Add 10 μL of each phage

dilution to each bacteria tube, vortex, and incubate at room temperature for 5 minutes. Remove 2 to 3 plates at a time to prepare for titer. One at a time, transfer the 205 μL of infected bacteria cells to a culture tube with agarose top, vortex quickly, and immediately pour onto a pre-warmed LB/IPTG/Xgal plate. Spread agarose top evenly and allow to cool for 5 minutes. Invert and incubate plates overnight at 37°C.

Amplification of Biopan

Start an overnight culture. On the next day, dilute overnight culture 1:100 in LB (200 μL in 20 mL of LB) and add 20 to 50 μL of eluate to the dilution and incubate at 37°C on shaker for 4.5 hours. Transfer the culture to an oakridge centrifuge tube and spin for 10 minutes at 10,000 rpm at 4°C. Transfer the supernatant to a fresh tube and spin again. Pipet/pour the upper 80% (usually 16 mL) to a fresh tube and add 1/6 its volume of PEG/NaCl (usually 2.7 mL). Allow phage to precipitate overnight at 4°C. The next day, spin PEG precipitation for 15 minutes at 15,000 rpm at 4°C. Discard supernatant, re-spin, and remove residual supernatant with pipette. Suspend the pellet in 1 mL of TBS. Transfer the suspension to a microcentrifuge tube and spin for 5 minutes at 4°C to pellet cells. Transfer liquid to a new tube and add 1/6 the volume of PEG/NaCl (usually 167 μL). Incubate on ice for an hour. Centrifuge tube for 10 minutes at 4°C. Discard supernatant, re-spin, and remove residual supernatant with pipette. Suspend the pellet in 200 μL of TBS. Titer the amplified phage, usually plating 10^{-6}, 10^{-7}, and 10^{-8}. Calculate the concentration and for the next round of biopanning, make sure the number of input phage is consistent around 2×10^{11}.

RESULTS

CdSe/ZnS Layer-by-Layer Modification

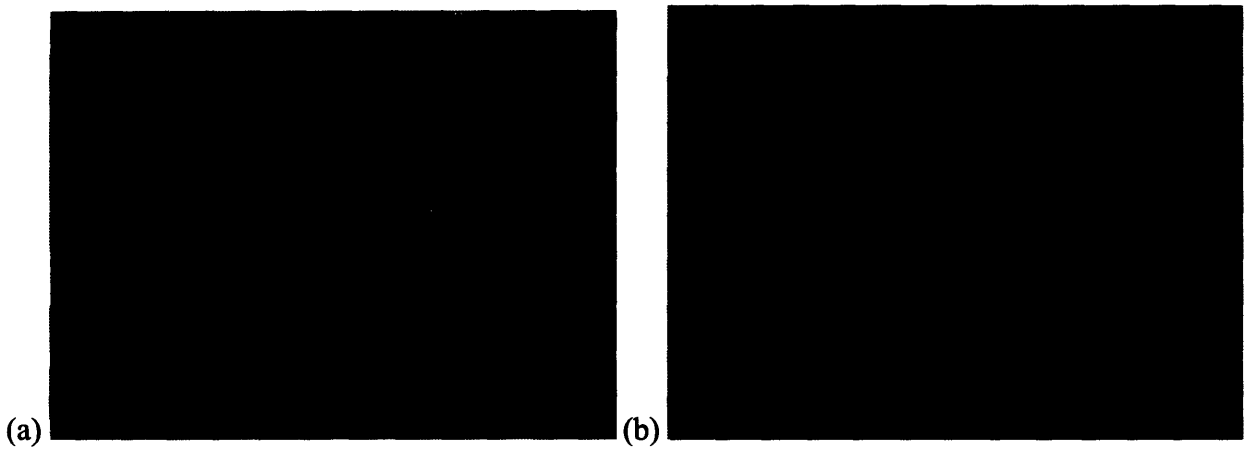


Figure 3. Single Layer of Red and Green CdSe/ZnS Quantum Dots. (a) A polydimethylsiloxane (PDMS) stamp with square features was used in this single layer of red QDs. The layer-by-layer method produces blanketing fluorescence in the entire image suggesting that hyaluronic acid (HA) did not coat evenly on glass substrate. This image was viewed using a red filter. (b) The same stamp is used for a single layer of green QDs and a similar blanket appears under the green filter.

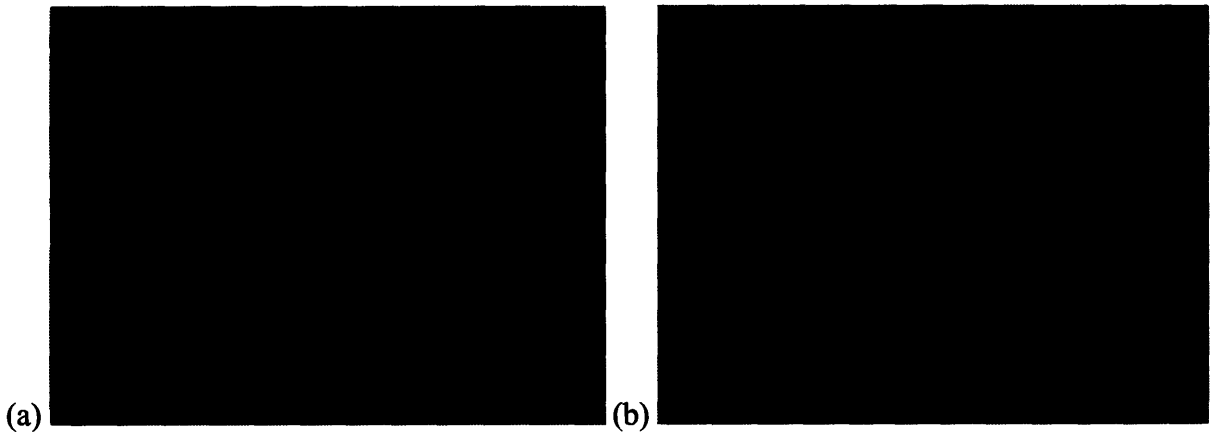


Figure 4. Bottom Layer of Red and Top Layer of Green CdSe/ZnS Quantum Dots. (a) A polydimethylsiloxane (PDMS) stamp with square features was used in this double layer of CdSe/ZnS QDs. The red layer is on the bottom and can be seen using a red filter. Again there is a background of red QDs in the squares where there should be nothing. (b) The green QDs were deposited on top of the red QD layer and visualized using a green filter. The blanketing effect is noticeable here because of the saturation and evenness of green QDs in all regions.

Spincoating and Dropcasting

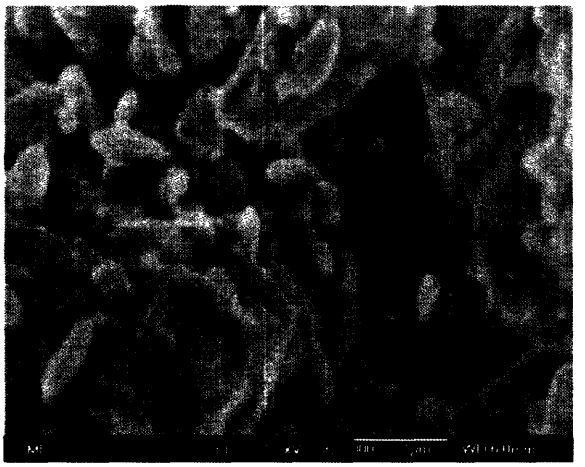
(a)  (b) 

Figure 5. Scanning electron microscope (SEM) images of Jifa GaN Quantum Dots. (a) Jifa GaN batch 0720 contained a large amount of trioctylphosphine oxide (TOPO) and was spin-coated at 1000 rpm for a minute while suspended in chloroform onto glass. (b) Jifa GaN batch 1005-1 was washed in methanol, then dropcasted on glass, and annealed.

TABLE 1. X-ray Photoelectron Spectroscopy (XPS) Results on the Ratio of Elements to Gallium on Sample Surface. (a) Jan 25-27 data shows that a methanol wash reduced the amount of organics, or carbon on the GaN surface. (b) Feb 15 data shows that a methanol wash increased the amount of carbon present on the sample surface.

(a)

	untreated	MeOH wash
Ga 2p	1	1
O	2.7	2.9
C	3.17	1.9

(b)

	untreated	MeOH wash
Ga 2p	1	1
O	3.8	5.31
C	9.67	13.03

TABLE 2. X-ray Photoelectron Spectroscopy Results on the Ratio of Elements to Gallium on Sample Surface for Three Washes. All samples were first washed with methanol. Two received more etching treatment: one with nitric acid (HNO_3) and the other with hydrochloric acid (HCl). The hydrochloric acid was most effective in reducing the amount of carbon on the GaN surface.

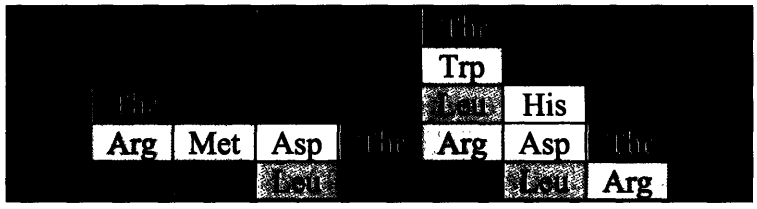
	MeOH	HNO_3	HCl
Ga 3d	1	1	1
O	6.55	4.7	3.72
C	14.23	12.51	4.52

TABLE 3. X-ray Photoelectron Spectroscopy Results on the Ratio of Elements to Gallium on Jifa GaN batch 0720 Surface. This batch was made with a lot of trioctylphosphine oxide (TOPO) as seen in the extremely high ratio of carbon to gallium.

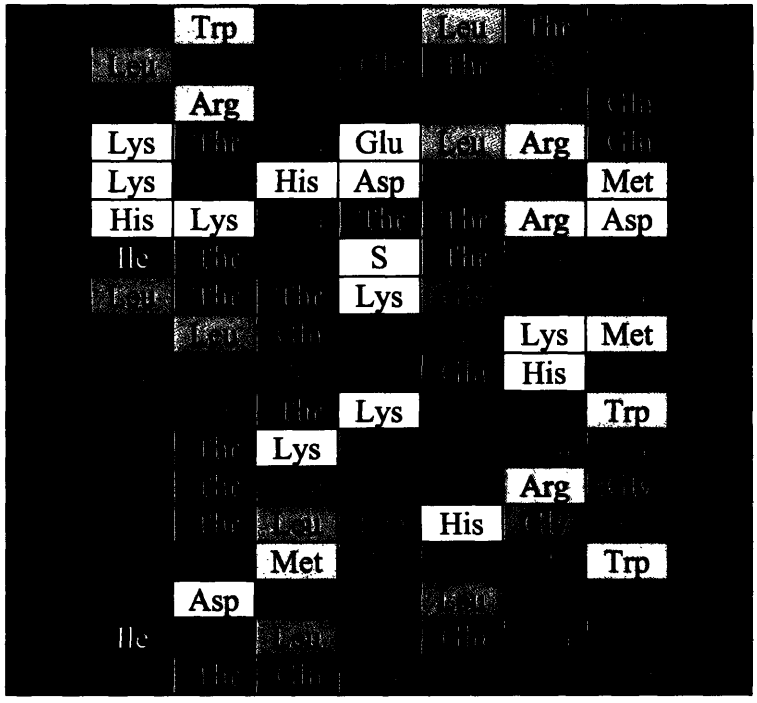
Ga 2p	1
O	13.21
C	59.86

Biopanning Sequences

(a)



(b)



(c)

	Glu	His	Lys		Thr	Glu
Gly	Leu	Leu		His	Arg	His
	Gly			Leu		
			Leu		His	Leu
	Thr	Arg	Ile	Gly	Asp	Lys
	His		Gln		Leu	Thr
		Asp	Arg		Arg	
	Glu	His	Lys		Thr	Glu
Gly	Leu	Leu		His	Arg	His
	Gly			Leu		
			Leu		His	Leu

(d)

	Glu	His	Lys		Thr	Glu
	Glu	His	Lys		Thr	Glu
Ile		Pro	Thr	Glu	Ser	Ile
	Glu	His	Lys		Thr	Glu

Figure 6. Biopanning Results using M13 Phage and the New England Biolabs pIII Constrained 7-Amino Acid Library. (a) Sequences for the first round of commercial GaN. (b) Second round of commercial GaN sequences. (c) Third round of commercial GaN sequences. There is still no consensus sequence at this round. There are several duplicates in this round. (d) Round 1 of Jifa GaN. There is a sequence in triplicate in this round that also matches one in the third round of the commercial GaN.

DISCUSSION

Surface Ligand Exchange of Jifa GaN Quantum Dots

When trying to apply the same surface ligand exchange that was effective for CdSe/ZnS QDs for Jifa GaN QDs, the GaN did not bind to MAA. This result is due to the differences in surface chemistry of ZnS and GaN. GaN is a stable material and nitrogen/sulfur (N-S) bonds are weak compared to disulfide bonds. In the ligand exchange it is possible that MAA does not form a sufficiently strong bond with GaN and is easily displaced by solvent interactions. Though it is possible to change the binding molecule, MAA, it is still difficult to judge the success of other molecules because GaN is stable and unreactive.

In addition, the GaN surface ligand exchange experiments resulted in a loss of GaN QDs. Though the MAA did not allow GaN to become water-soluble, it was still difficult to precipitate the GaN from excess MAA. Dialysis was used to separate GaN and MAA, but afterwards, the GaN agglomerated and remained caught in the dialysis membrane.

It is clear that the surface chemistry of CdSe/ZnS and GaN QDs are different and a process like ligand exchange does not translate. It may not be necessary to use ligand exchange as the sole method for creating water-soluble GaN QDs. There is some current work in the lab to develop water-soluble GaN QDs by using micelles as well as using amphiphilic polymers [8].

CdSe/ZnS Layer-by-Layer Modification

In Figure 3.a the single layer of red CdSe/ZnS QDs did not deposit evenly in the regions separating the squares, where there should have been an absence of QDs. The hydrophobic PDMS stamp should push the negatively charged HA from underneath the stamp into grooves where the QDs will later deposit. From Figure 3.a it is evident that not all of the HA is pushed into the grooves because there are still circles of QDs in the center of the square features. Additionally, there is a high concentration of HA and therefore red QDs at the square borders suggesting that the aspect ratio of this PDMS stamp may not be tailored for even coating. HA forming this square border may indicate that the stamp grooves are too deep and that the aspect ratio would need to be changed for even spreading of QDs.

The same phenomenon can be seen for the green CdSe/ZnS QDs in Figure 3.b. Both samples also include a blanket background of QDs, which may be due to excess in HA or PDMS stamps with an aspect ratio in the grooves that does not facilitate the removal of HA beneath the square features.

When depositing a second layer of QDs Figure 4.a should be similar to Figure 3.a since the samples are both the bottom layer. However, the region of observation under the microscope may vary, reflecting differences in HA thickness on the sample when they were spin-coated. The center of the sample would have a higher concentration of HA than the outer edges and more

Spincoating and Dropcasting

Because the GaN QDs could not be made water-soluble at the time, alternative methods for depositing layers were examined. The synthesis of GaN involves TOPO covering the QD surface, which allows the particles to be soluble in organic solvents such as chloroform. Jifa GaN batch 0720 was synthesized with excess TOPO as seen in Table 3 where the ratio of carbon to gallium on the sample surface was 59.86:1. The large quantities of carbon can be attributed to the organics used in synthesis as well as TOPO.

The data from Table 3 corroborates the micron-sized features seen in Figure 5.a though the GaN should be on the nanometer scale. Large amounts of organic materials on the surface of the GaN during synthesis and storage may have caused agglomeration of nanoparticles. The nitrogen source during the synthesis is triethylamine, that is three ethyl molecules, which are short carbon molecules, per nitrogen. The temperature for synthesis is also approximately 230°C, high enough such that chloroform may break down, leaving dark brown residues that are indicative of carbon. Because the synthesis occurs in a closed system, byproducts like chlorine gas are not allowed to escape during the reaction.

Dropcasting the Jifa GaN batch 1005-1 in Figure 5.b also yielded similar micron-sized structures even though this batch did not have excess TOPO.

Removal of Organics on GaN Surface Using Methanol and Acid Washes

Several liquids were used to remove the organics on the surface of GaN. As seen in Table 1, it is inconclusive whether methanol is successful at reducing the amount of carbon on the surface. The data taken on January 26 and 27 in Table 1.a shows the ratio of carbon to gallium after a methanol wash to be 1.9:1, which is 40% less than the untreated sample with a ratio of 3:17:1. The data taken from February 15 in Table 1.b shows that the ratio of carbon to gallium increased by 35% after a methanol wash from 9.67:1 to 13.03:1. More data points would need to be documented before a final conclusion can be made as to the efficacy of methanol.

When comparing methanol, nitric acid, and hydrochloric acid in Table 2, it has been shown through XPS that hydrochloric acid effectively removes carbon compounds on the GaN surface. All the samples were pre-washed in methanol. The nitric acid reduced the ratio of carbon to gallium from 14.23:1 with the methanol wash to 12.51:1, a 12% decrease. The hydrochloric acid was even more effective than nitric acid, with a total reduction of 64% from 14.23:1 to 4.52:1.

Biopanning Sequences

The biopanning procedure included a methanol wash because it was believed to remove excess organics like TOPO from the surface of the GaN so that the phage sequences would be targeting GaN surface chemistry rather than having TOPO selectivity.

The preliminary data for the commercial GaN was completed for three rounds, but no consensus sequence has come up and will need to be repeated for a fourth round. In past biopanning data that used bulk GaN substrates and commercial GaN powder as the material of interest, the amino acid residues that were sequenced were primarily hydrophobic. For these

sequences the pIII unconstrained twelve amino-acid M13 library was used. The DNA sequences in Figure 6.a-c, however, have a mixture of hydrophobic and hydrophilic residues.

The first round of Jifa GaN batch 1005-1 was sequenced and resulted in three of the same sequence. This triplicate could be due to contamination, that is, that the particular sequence Cys-Asn-Gln-His-Lys-Ser-Thr-Gln-Lys in Figure 6.d amplifies faster than other sequences even though a random sampling of sequences was used.

This same sequence is also seen twice in the third round of commercial GaN, potentially indicating that the surface chemistries of commercial GaN and methanol-washed Jifa GaN are similar. It is still early to make this conclusion particularly because three rounds have not been conducted for the Jifa GaN and there was no consensus sequence that had been shown for the commercial GaN.

After the biopanning results have been sequenced, it is necessary to determine the affinity strength of particular sequences.

FURTHER WORK

Further work in this group is being conducted on understanding the surface chemistry of the Jifa GaN and to develop methods for making the nanoparticles water-soluble. In addition, the purification of GaN QDs by removing residual organic materials is necessary for making layers of these particles. The biopanning work needs to be completed as well. It has been shown that viruses self-assemble into crystalline films that can bind nanomaterials, including cobalt. Using this technique, the virus template can be used to quantify electronic behavior of GaN QDs and make devices.

Long-term prospects include the fabrication of bulk GaN using the QDs, which have additional bandgap tuning from that results from their size and quantum confinement. This

process may be preferred to current methods of synthesis involving metalorganic chemical vapor deposition which is a slow and expensive process.

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