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LDRD PROJECT NUMBER: 222478

LDRD PROJECT TITLE: Novel In-situ Patterning Technique to Fabricate Single Quantum Dots for Quantum Photonics

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ABSTRACT:

Photon sources able to emit single or entangled photon pairs are key components in quantum information systems. Semiconductor quantum dots (QDs) are promising candidates due to their high efficiencies and ease of integration with other photonic or electronic components. State-of-the-art QDs, however, are limited to certain emission wavelengths and specific applications due to material choice constraints and their randomness in shape/size. This project is focused on developing a novel in-situ patterning technique to realize QDs with a broad emission range, shape/size control and the ability to emit single/entangled photons.

Our approach has two key elements: (1) In-situ patterning via arsenic-induced nanovoid etching on antimonide surfaces and (2) In-filling of nanovoids to form QDs. By closely controlling the experimental conditions, it is shown that this technique can be used to realize III-V QDs in As_2-etched nanovoids on a GaSb surface. The exposure to As_2 in terms of substrate temperature, time and flux is found to have a significant impact on the process variables such as nanovoid depth, QD dimensions etc. An in-depth analysis of the etch mechanism reveals that by controlling the As_2 exposure, uniform 3-dimensional nanostructures with varying areal densities can be obtained without an in-filling step. Preliminary optical characterization of these nanostructures shows that these QDs may be relevant for realizing emitters in the telecom wavelength range.

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INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS:

Reliable single-photon sources (SPS) are crucial to the implementation of several quantum technologies including communication, computing, cryptography, and sensing. Among other approaches (organic molecules, color centers, carbon nanotubes), semiconductor QDs have demonstrated on-demand generation of single photons and entangled photon pairs, with high indistinguishability, emission efficiency, purity, and record brightness[1-4]. At present, QDs realized from epitaxial growth of III-V semiconductors exhibit the best performance. There are two state-of-the-art approaches for obtaining III-V QDs for use in SPS: Stranski-Krastanov (S-K) and droplet epitaxy (DE). S-K is based on lattice mismatched heteroepitaxy where the strain between the epilayer (QD) and the substrate drives 3-dimensional growth. For example, InAs grown above a certain critical thickness on GaAs (~7% lattice mismatch) forms QDs. In (Ga)As QDs grown using the S-K growth mode have been successfully used for decades in many devices including lasers[5], detectors[6] and single-photon emitters[1,2]. However, there are fundamental drawbacks of these QDs that limit their performance in SPS: (i) The growth process is entirely based on self-assembly and this limits control over size/density/position and introduces a certain degree of randomness (ii) the need for strain to cause QD growth limits the number of available material combinations and in turn, limits the emission range accessible to S-K QDs. On the other hand, the DE method uses the controlled crystallization of metal droplets on III-V surfaces to form QDs[7,8]. While DE QDs offer additional advantages over S-K, they require complex growth recipes and are plagued by low brightness.

The hypothesis for this project is based on the idea that in order to control the size/density/position and not be limited by material availability, the QD growth needs to be carried out on a prefabricated pattern. The pattern (usually holes with set dimensions) then dictates the structural characteristics and any material of choice can be used to "fill" the pattern and form QDs. This idea has been attempted with two different approaches: (i) InAs QDs where the substrate is pre-patterned using lithography techniques before epitaxial growth[9,10]. However, it was found that the proximity of the QDs to pre-processed interfaces drastically reduces their quantum efficiencies due to defects and contaminants. (ii) A recent modification to the DE method called local droplet etching (LDE) [11]uses metal droplets (Ga, In or Al) to etch voids on III-V surfaces that are then in-filled to form QDs. This circumvents the need for strain and the material choice limitations in S-K QDs but at the same time introduces complications involving the removal of droplet material after the nanovoids are formed. Besides, LDE QDs also exhibit low brightness metrics.

In this context, the R&D for this project seeks to answer the following questions:

1. Can an alternative technique be developed for realizing III-V semiconductor QDs suitable for use in SPS?

2. If patterning is used, how can the drawbacks of ex-situ patterning such as defects & contaminants be avoided?
3. Will this technique alleviate the limitations of current methods? Is it possible to have control over size/shape/ density and not be constrained by material choices?
4. If QDs are obtained (structurally verified), can their optical characteristics be quantified? in terms of emission wavelength, linewidth, brightness etc.

The central idea in this project is to use an arsenic molecular flux on an antimonide-based surface to etch nanovoids which can then be in-filled to form QDs. The arsenic dimer molecule (As_2) is commonly used in III-As epitaxial growth and so, the patterning (etch) part of the process can be carried out in-situ without introducing interfacial defects. The combination of etch and in-fill procedures presumably offers control of size, shape, and density of the QDs without any material choice limitations. Unlike LDE, this method does not involve the use of metal droplets for the etch.

An array of epitaxial growth conditions and structural details are optimized as part of this study. The results can be summarized as follows:

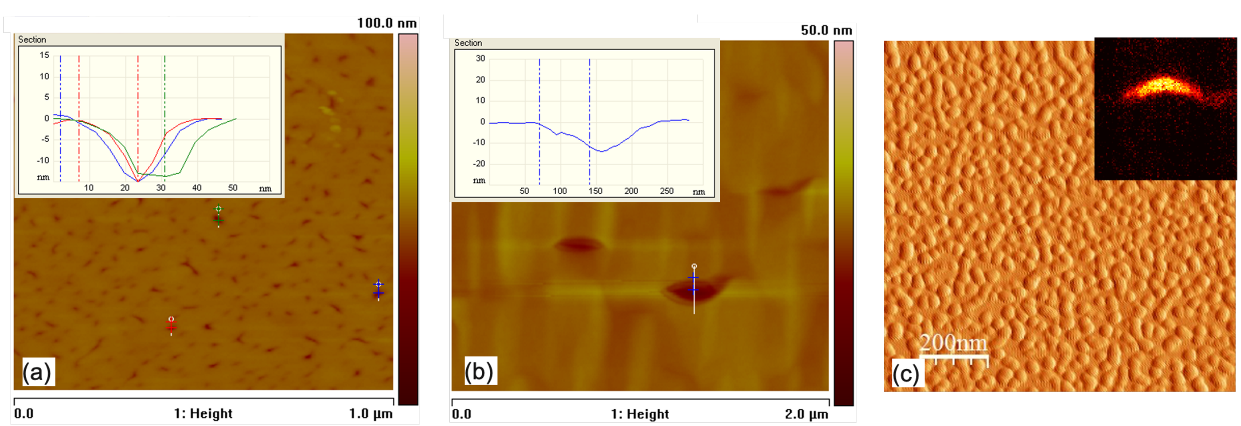


Figure 1. (a) 1 X 1 µm AFM scan with a line profile analysis of As_2-etched nanovoids on GaSb surface (b) 2 X 2 µm AFM scan and line profile analysis of an infilled nanovoid (c) 1X 1µm AFM scan and GaAs-component cross-section TEM image (inset) of arsenic-assisted QD formation.

(A) Under adjusted growth conditions (As_2 exposure, substrate temperature etc) nanovoid formation was observed on GaSb surfaces - figure (a)
(B) Nanovoid size and density can be controlled based on growth conditions. Figure (b) shows a larger (compared to figure a) nanovoid in-filled with a GaAs QD.

as observed in figures (a) and (b), the size/shape uniformity is poor, which is not favorable for the applications of this project. A follow-up study aimed at improving the uniformity revealed an unanticipated feature of the As_2 etch on III-Sb surfaces: nanostructure formation without etch+infill.

(C) If the As_2 exposure step is carefully controlled, QD formation can be realized without the etch-in-fill process. The material composition of these QDs is found to be mostly GaAs.

This offers an alternative QD growth method where neither strain nor the etch-infill process is required.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY:

The epitaxial growth described in this project was carried out using molecular beam epitaxy (MBE) on (100) GaSb substrates. The substrate temperature was measured using a pyrometer and the growth rates were calibrated and monitored using reflection high-energy electron diffraction (RHEED). The MBE systems were equipped with valved cracker sources for both arsenic and antimony, affording precise control over both fluxes.

Growth process: The surface oxide on GaSb substrates was first thermally desorbed at ~540^{0}C for 15 min. The substrate temperature was then adjusted to 510-520^{0}C and a smoothing layer of GaSb was grown. Following this, the substrate temperature was adjusted for the As_2 etch process (if needed) and the GaSb surface was exposed to a controlled As_2 flux. The beam flux monitor (BFM) equivalent pressures for As_2 were in the range of 7E-7 and 1E-5 Torr and the exposure time was varied from 60s to 600s. The As_2 etch was followed by a 300s Sb soak to aid the formation of the voids or QDs. The structure is completed with the growth of a GaSb cap on top. For atomic force microscopy (AFM) samples, the etch process (As_2 etch followed by 5 min Sb soak) was repeated at the terminating top GaSb surface. For photoluminescence (PL) samples, a $Al_{0.5}Ga_{0.5}Sb$ barrier layer was used to embed the QDs.

Characterization: The nanovoid and QD dimensions were measured mainly using AFM on a Veeco Dimension 3100 system. Lift out of a sample for transmission electron microscopy (TEM) was achieved using a Thermo Fischer G3 Helios dual focused ion beam. To protect the QDs at the surface of the sample, a thick carbon layer was deposited using the electron beam followed by a Pt deposition with the electron beam. Final thinning was done at 2 kV with progressively lower currents (down to 48 pA) to avoid curtaining and amorphous damage. TEM was performed using a FEI Titan G2 8200. TEM was used to analyze the cross-sectional profile and coupled with energy dispersive x-ray analysis (EDX) to deduce the material composition of the QDs. The composition profile was also looked at using secondary ion mass spectrometry (SIMS) measurements carried out by Evans Analytical Group (EAG). PL measurements were done at ~8K using a standard lock-in technique with a 632nm pump and an InGaAs detector.

Nanovoid etch: The nanovoid etching process is based on As_2 aggressively reacting with GaSb according to the following reactions[12]:

$$2GaSb + As_2 \rightarrow 2GaAs + Sb_2 \quad \Delta H^0 = -47.6\ kJ/mol$$

$$GaSb + As_2 \rightarrow 2GaAs + AsSb \quad \Delta H^0 = -33.9\ kJ/mol$$

Note that the enthalpy is negative for both the anion exchange (1) and the isoelectronic AsSb compound formation (2) reactions. The strong reaction of As_2 exposure to GaSb surfaces has previously been observed [13], but not in the context of in-filling QDs. Based on the results from this study, the As_2 exposure leads to the formation of highly faceted nanoscale pits, as shown in figure 1(a) above.

QD in-filling: Once the nanovoids are etched, they can be in-filled with any material to form QDs. We chose GaAs to be the filled QD material for demonstrating the technique. This choice was primarily based on the ease of growth and to be analogous to GaAs QDs that are grown in metal droplet-induced nanovoids using the LDE method [11].

The challenge here is to ensure that the QD material is only deposited in the nanovoid and not on the planar surfaces around it. This is done by using migration enhanced epitaxy (MEE). The MEE process involves providing an alternate supply of constituent elements to the substrate. So, instead of simultaneously exposing the nanovoid surface to both Ga and As_2 fluxes, the GaAs QDs are formed by a periodic supply of Ga only followed by an As_2 soak. This effectively enhances the surface migration of Ga and supports the energetically favorable growth of GaAs inside the faceted voids instead of on the planar (100) surface. The growth times used here were 0.5s of Ga and 10s of As_2. The thickness of the QD is controlled only by the Ga deposition times and the number of periods is accordingly adjusted. MEE has been used previously to achieve selective epitaxial growth in GaAs and other material systems[14].

As_2-etched QD formation: As part of the project, a complex grid of growth conditions (temperature, flux, growth rate etc.) were optimized for both the nanovoid etch and the QD-infilling processes. During this study, it was found that a controlled As_2 etch of an antimonide surface (nominally GaSb) leads to the formation of 3-dimensional structures without nanovoid etching and in-filling. The procedure here is similar to the nanovoid etch where the GaSb surface is exposed to a 60s As_2 flux, followed by a 300s Sb soak. The nanostructure formation is only observed at very low As_2 exposures (details included in the Results section). For PL and TEM samples, a 4nm GaSb layer is grown on the $Al_{0.5}Ga_{0.5}Sb$ lower barrier. This 4 nm layer is etched with As_2 and followed up with a top $Al_{0.5}Ga_{0.5}Sb$ barrier. For surface QDs, a terminating 4 nm GaSb layer is deposited after the top barrier and etched with As_2.

RESULTS AND DISCUSSION:

The strategic plan for the project defined two success metrics:

- Nanovoid formation through As_2 etch
- Nanovoid in-filling to form GaAs QDs

Figure 2 below shows a 1X1 µm AFM image of an As_2-etched GaSb surface (a) along with a line scan (b) for specified contours. The substrate temperature for the etch was 520^{0}C and the As_2 exposure time was 10 min. The line scans clearly show the formation of nanovoids with typical dimensions of ~15nm depth and a width of ~40nm. It is to be noted that the void formation was only observed at "high" As_2 exposures i.e., at BFM values > 2E-6 Torr and etch times > 10min. The density of nanovoids on the surface is ~300/µm^2 with very low uniformity in size and shape across the surface.

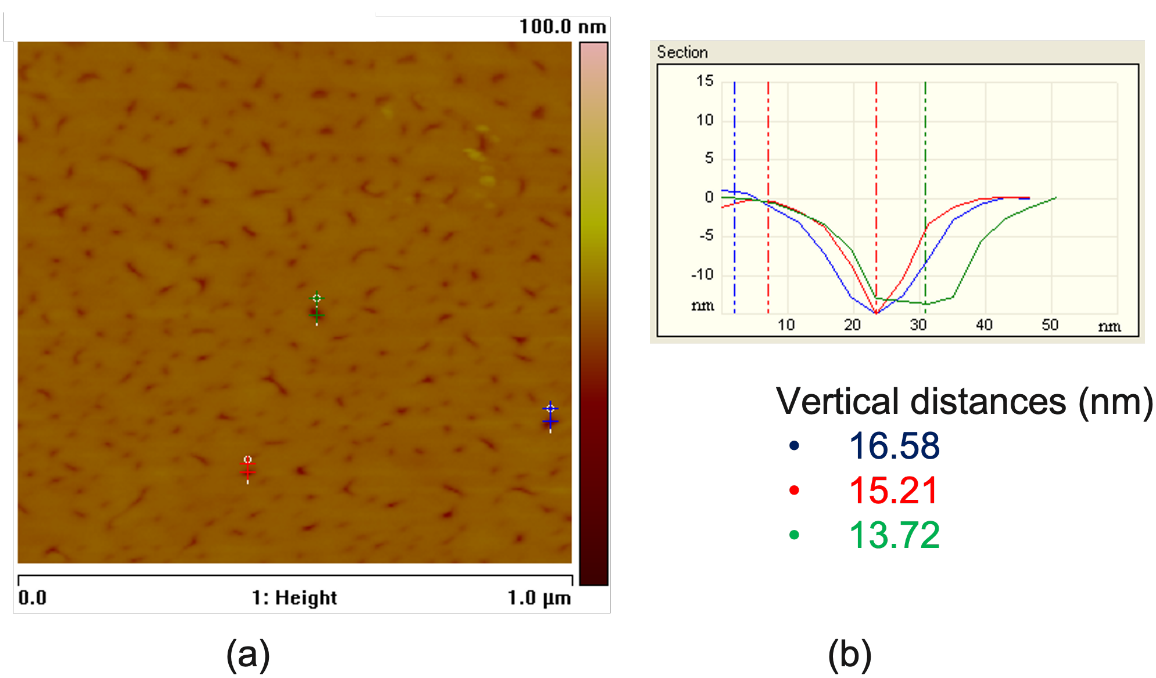
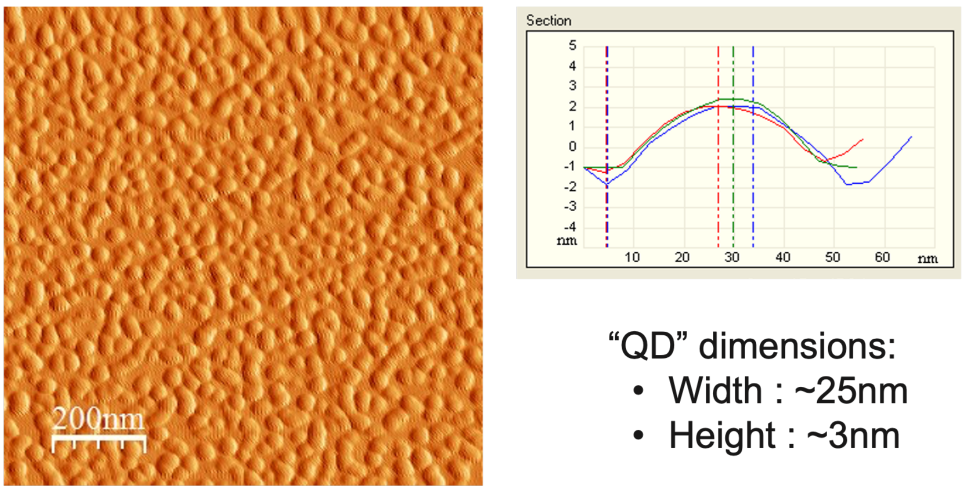


Figure 2. (a) 1 X 1 µm AFM scan with (b) a line profile analysis of As_2-etched nanovoids on GaSb surface – high exposure

While determining the growth conditions required for nanovoid formation, a separate As_2 etch regime is observed. At "low" exposures (BFM: 1E-6 Torr; Time: 60s or less) of As_2 the etched GaSb surface forms 3-dimensional nanostructures instead of voids. Figure 3 shows a 1X1µm AFM image and corresponding profile analysis of a GaSb surface etched with low As_2 exposure. The nanostructures are tightly packed (areal density: ~600/µm^2) with typical dimensions of 3nm height and ~25nm width. Their dimensions/density are very similar to high-density InAs QDs grown on GaAs using the S-K method.



(a) (b)

Figure 3. (a) 1 X 1 µm AFM scan with (b) a line profile analysis of As_2-etched nanovoids on GaSb surface – low exposure.

The etch regime on the GaSb surface is found to be heavily dependent on the As_2 exposure. Note that the As_2 exposure on the surface is a combination of arsenic BFM values, time, and substrate temperature. A lower substrate temperature means a higher sticking coefficient for As_2 leading to a higher exposure, and vice versa. From a set of samples grown at different growth temperatures with different As_2 etch times and BFM values, an outline of the different etch mechanisms can be understood. This trend is illustrated in AFM images shown in figure 4. At very low As_2 exposures, the etch process leads to the formation of 3-dimensional nanostructures at a low areal density (figure 4a). As the exposure increases (moving rightward), first the density of the nanostructures increases, followed by a slow coalescence of the islands, and finally forming nanovoids at the highest exposures (4f). Also note that the island coalescence and the initial formation of nanovoids is oriented along a specific crystallographic direction $(1\bar{1}0)$. This can be explained based on the direction dependence of surface mobility of the adatoms, which is higher in this specific direction.

The potential of an As_2 etch yielding nanostructures with similar structural characteristics to S-K QDs is significant. This implies that a 3-dimensional growth mechanism can be triggered with only an exposure, without strained growth and without the need for etching nanovoids and infilling them. Moreover, figures 4 (a) and (b) suggest that the size and density of the nanostructures can be controlled by the simply tuning the exposure. The remainder of the results focus on deducing the characteristics of these nanostructures formed by low As_2 exposure and are henceforth referred to as "As_2-etched QDs."

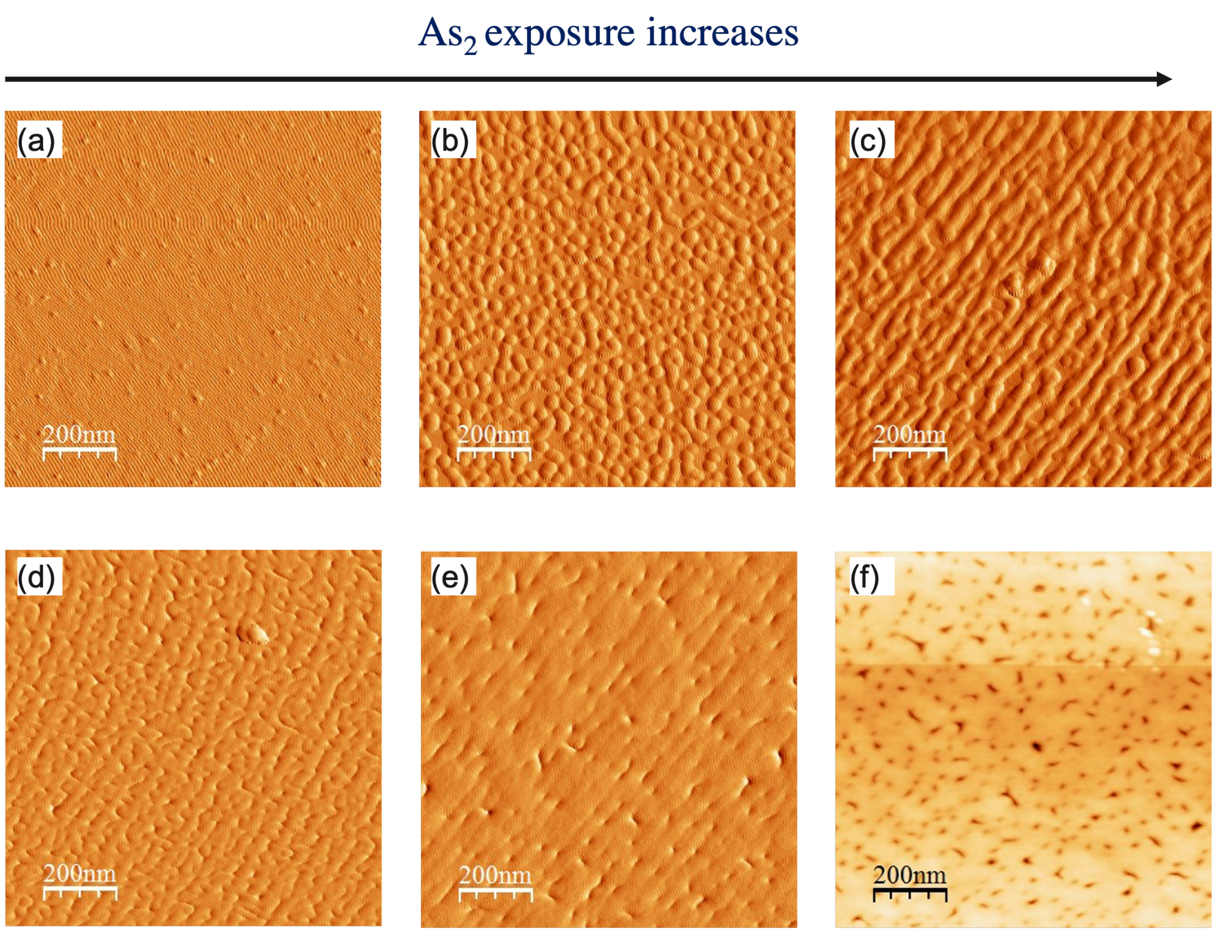
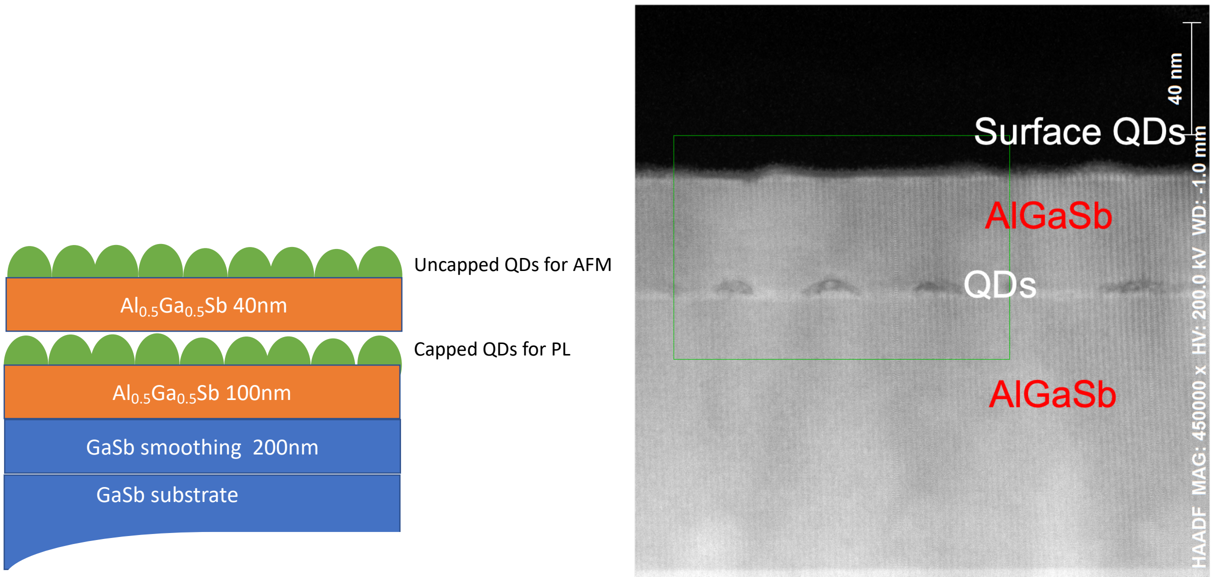


Figure 4. 1 X 1 μm AFM scans of GaSb surfaces etched with increasing As_2 exposures (a-f)

To study the material composition and cross-sectional structural characteristics of the As_2-etched QDs, a combination of SIMS analysis and TEM is employed. The structure used here is described in the methodology section and is shown in figure 5 (a). Assuming that the QDs are composed of some intermediate Ga(As)Sb alloy, $Al_{0.5}Ga_{0.5}Sb$ is chosen as a higher bandgap barrier and to also provide good contrast for imaging the QDs using SIMS and TEM.

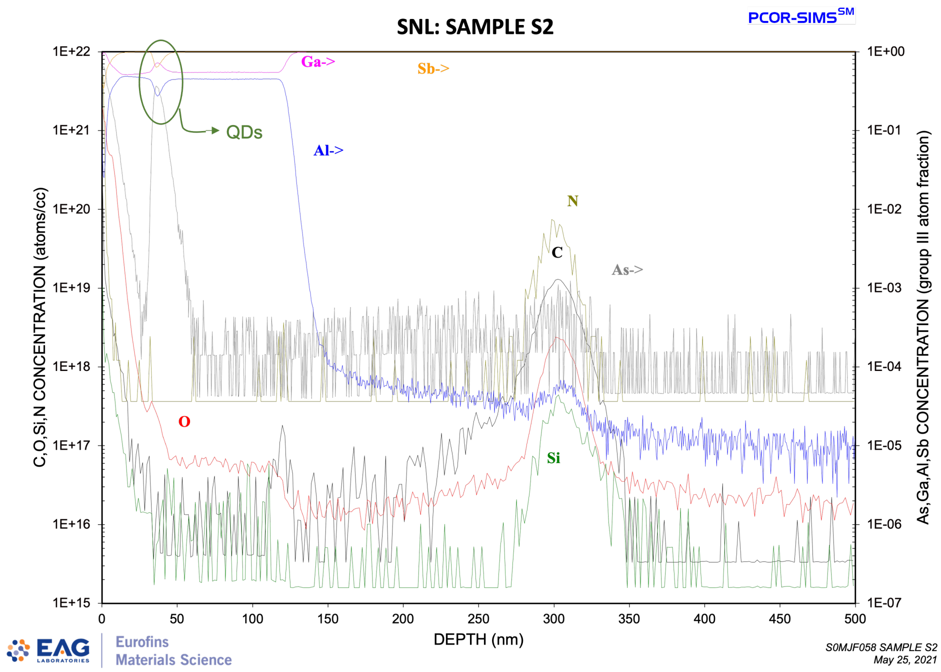


(a) (b)

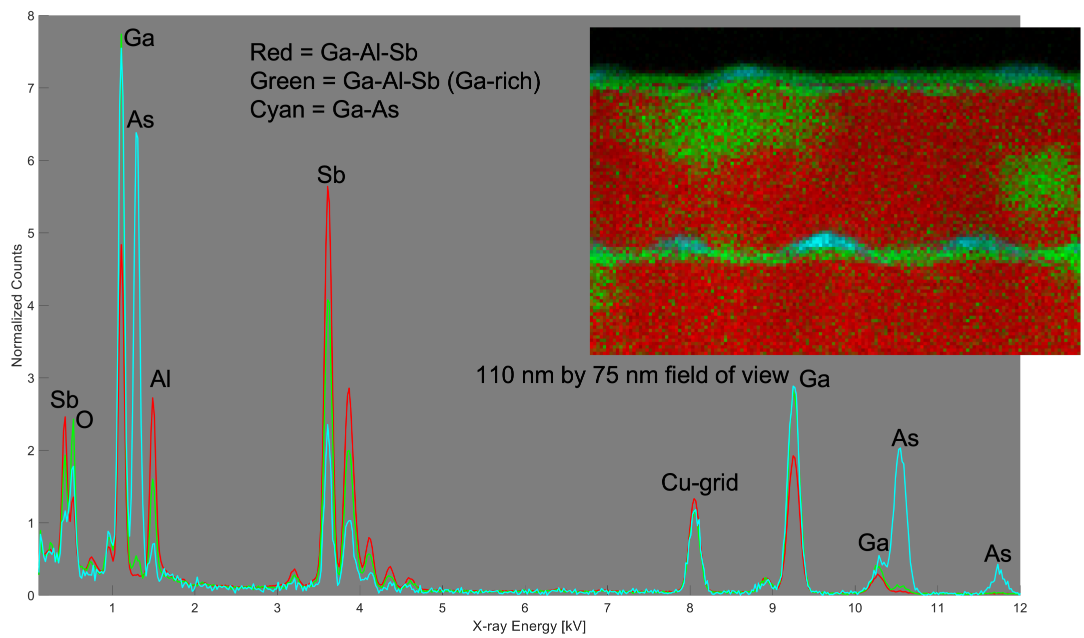
Figure 5. (a) Schematic of structure used for SIMS, TEM and PL measurements.
(b) Corresponding cross-sectional HAADF STEM image of the structure.

Figure 5(b) is a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the As_2-etched QDs from a cross-sectional view. It clearly shows 3-dimensional nanostructure formation without any significant defect propagation through the structure. The dimensions and the areal density of the QDs agree well with approximations from AFM scans. The material composition of these QDs is investigated using both SIMS and EDX, as shown in figure 6 below. Although the thickness of the QD layer (< 4nm) is right at the limit of measurement for SIMS, figure 6 (a) shows a thin layer where the Sb fraction dips and the As composition has a peak. This GaAsSb layer is ~40nm (as expected) from the surface (marked in green). EDX gives a better estimate of the QD composition and is shown in figure 6 (b). According to EDX profiles, the QDs have a GaAsSb (<50% Sb – cyan) tip and a thin GaSb layer (green) underneath. The red-colored layers are the $Al_{0.5}Ga_{0.5}Sb$ barriers and may have some areas (shown in green) where there is FIB damage to the TEM sample.

PL measurements (not shown here) were carried out on the structure, but the results weren't conclusive. A peak is observed at ~1550nm and we suspect this could be attributed to the thin GaSb layer underneath the QDs.



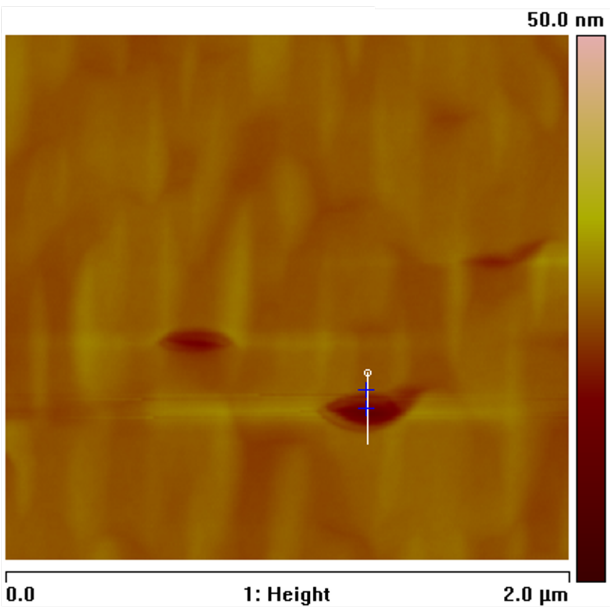
(a)

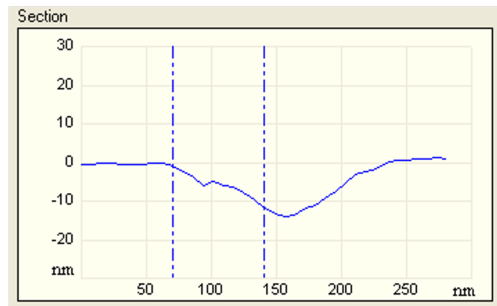


(b)

Figure 6 (a) SIMS analysis results and (b) EDX profiles for the As_2 etched QD

For proof of concept, the MEE method to in-fill the nanovoids was attempted on LDE QDs. Figure 7 shows a 1X1 µm AFM image of a typical void in-filled with GaAs along with a line profile scan. The void dimensions are reasonable, and the line scan shows a small bump inside the void, revealing the in-filled GaAs.





- Depth: ~15nm
- QD height: 7-8nm

Both nanovoid and QD-infilling were obtained by carefully adjusting the growth conditions. However, the most significant result is the realization of 3-dimensional nanostructures on antimonide-based surfaces using only an As_2 etch. Depending on the actual composition of the QDs, they could be relevant to developing emitters at the two telecommunication wavelengths, 1.3µm and 1.55µm. The results also reveal that this method offers control over the size (possibly shape) and areal density of the QDs. This work builds on previous efforts by Huang et al. [13] where the nanovoids were observed but the etch mechanism wasn't fully understood.

ANTICIPATED OUTCOMES AND IMPACTS:

Work done under this project covered the structural aspects of both the nanovoid + infilling QDs and the As_2-ecthed QDs. The next step, from a material science perspective is to conduct a comprehensive optical study of both nanostructures to deduce emission efficiencies, carrier lifetimes and dimensionality. We intend to propose this as a future LDRD project and believe the findings will be relevant to multiple investment areas including Material Science, Nanodevices and Microsystems, and New Ideas. Assuming that the QDs show a reasonable optical signature, the project idea could also include a device aspect where the nanostructures can be used as emitters and integrated with other technologies including metasurfaces, photonic crystal cavities etc.

A publication detailing the findings presented here is in the draft stage and progressing towards peer review. The title for the manuscript is, "III-AsSb nanostructures formed by arsenic-assisted surface etching" and will be relevant to both physics and material science journals. A follow-up publication including optical characteristics and a theoretical model to explain the As_2 etch mechanism is planned. We also plan to submit an abstract with these results for an oral presentation at the electronics materials conference (EMC) – due in January 2022. Additionally, a technical advance (TA) document describing the novel etch process that forms 3-dimensional nanostructures without the need for strained growth or nanovoid formation is being drafted.

To compare the work done here to state-of-the-art QD growth methods, time was invested in process development of both S-K and LDE QDs. These capabilities are now additions to the user program at the Center for Integrated Nanotechnologies (CINT) and has already led to interest and submitted user proposals from multiple universities and national labs.

Potential new R&D from this project can be pursued on different fronts. However, all options will depend on realization of some useful optical properties from the QDs discovered here. On the material science side, further work can be done to adjust growth conditions for better structural or optical properties. This project only explores the formation of As_2-assisted QDs on GaSb surfaces. We believe this mechanism can also be used on other III-Sb surfaces (AlInGaSb) to span a wide range of emission wavelengths. On the device side, the integration of these QDs on multiple platforms including lasers, detectors and single-photon emitters can be explored.

The results from this project can potentially be relevant to multiple existing Sandia programs in the field of quantum information science (QIS). Specifically, if the QDs emit in wavelengths of interest they can be integrated with studies that require efficient, tunable, high-brightness emitters. Additionally, user interest in this class of QDs can lead to external funding opportunities. More details are included in the Addendum section.

CONCLUSION:

The overarching goal of this project was to develop III-V nanostructure emitters that are capable of functioning as efficient SPS. Our approach focused on epitaxial growth of QDs and was based on the hypothesis that an in-situ patterning of the growth substrate followed by in-filling QDs offers control over size/shape/density and tunability in emission wavelength. We used As_2 molecules - that are known to aggressively react with III-Sb surfaces- to etch nanovoids in GaSb. The growth conditions (As_2 flux, temperature, etch duration) were optimized to form nanovoids and it was found that the As_2 exposure in general plays a consequential role in the etch process. While high exposures resulted in voids, lower controlled As_2 exposures revealed a unique etch mechanism that formed 3-dimensional nanostructures. It was also found that the exposure can be used to control the structural characteristics of the nanostructures. From compositional analysis, it was determined that the QDs are composed of GaAs(Sb) with an Sb composition < 50%. Preliminary PL measurements indicate that the QDs may emit in wavelength windows of interest to telecommunication technologies. The MEE procedure is used to verify GaAs QD growth in etched nanovoids.

The state-of-the-art methods to form III-V QDs include strained growth (S-K) and nanovoid etching followed by in-filling (LDE and part of this project). We demonstrate here an alternative technique where QDs can be realized through a simple etch process using As_2. The size/areal density can be tuned using the As_2 exposure and the emission wavelength can be adjusted by using a different etch template in the AlInGaSb quaternary material system.

REFERENCES:

[1] X. Ding, Y. He, Z.-C. Duan, N. Gregersen, M.-C. Chen, S. Unsleber, S. Maier, C. Schneider, M. Kamp, S. Höfling, C.-Y. Lu, and J. -W. Pan, "On-Demand Single Photons With High Extraction Efficiency and Near-Unity Indistinguishability from a Resonantly Driven Quantum Dot in a Micropillar," Phys. Rev. Lett. 116(2), 020401 (2016)

[2] H. Wang, H. Hu, T.-H. Chung, J. Qin, X. Yang, J.-P. Li, R.-Z. Liu, H.-S. Zhong, Y.-M. He, X. Ding, Y.-H. Deng, Q. Dai, Y.-H. Huo, S. Ho¨fling, C.-Y. Lu, and J.-W. Pan, "On-demand semiconductor source of entangled photons which simultaneously has high fidelity, efficiency, and in-distinguishability", Phys. Rev. Lett. 122(11), 113602 (2019).

[3] J. Liu, R. Su, Y. Wei, B. Yao, S. F. C. d. Silva, Y. Yu,J. Iles-Smith, K. Srinivasan, A. Rastelli, J. Li, and X. Wang, "A solid-state source of strongly entangled photon pairs with high brightness and indistinguishability," Nat.Nanotechnol. 14(6), 586-593 (2019).

[4] P. Senellart, G. Solomon, and A. White, "High-performance semiconductor quantum-dot single-photon sources," Nat.Nanotechnol. 12(11), 1026-1029 (2017).

[5] X. Wang, J. Ning, C. Zheng, and Z. Zhang, "Quantum Dot Materials Toward High-Speed and Ultrafast Laser Applications," Quantum Dot Optoelectronic Devices *27*, 207 (2020).

[6] A.D. Stiff-Roberts, "Quantum-dot infrared photodetectors: a review," J. Nanophotonics. *3*(1), 031607 (2009).

[7] K. Watanabe, N. Koguchi, and Y. Gotoh, "Fabrication of GaAs quantum dots by modified droplet epitaxy," Jpn. J. Appl. Phys. 39 (2A), L79 (2000).

[8] N. Koguchi, S. Takahashi, and T. Chikyow, "New MBE growth method for InSb quantum well boxes," J. Cryst. Growth 111(1-4), 688–692 (1991).

[9] S. Kiravittaya, H. Heidemeyer, and O.G. Schmidt, "Growth of three-dimensional quantum dot crystals on patterned GaAs (001) substrates," Physica E *23*(3-4), 253-259 (2004).

[10] L.N. McCabe, and J.M. Zide, "Techniques for epitaxial site-selective growth of quantum dots," J. Vac. Sci. Technol. 39(1), 010802 (2021).

[11] M. Gurioli, Z. Wang, A. Rastelli, T. Kuroda, and S. Sanguinetti, "Droplet epitaxy of semiconductor nanostructures for quantum photonic devices," Nat. Mater. 18(8), 799-810 (2019).

[12] M. Losurdo, P. Capezzuto, G. Bruno, A. S. Brown, T. Brown, and G. May, "Fundamental reactions controlling anion exchange during mixed anion heterojunction formation: Chemistry of As-for-Sb and Sb-for-As exchange reactions," J. Appl. Phys. 100 (1), 013531 (2006).

[13] S.H. Huang, G. Balakrishnan, M. Mehta, L.R. Dawson, D.L. Huffaker, and P. Li, "Arsenic-induced etched nanovoids on GaSb (100)," J. Appl. Phys. 102(4), 044312 (2007).

[14] Y. Horikoshi, "Migration-Enhanced Epitaxy and its Application," *Molecular Beam Epitaxy: Materials and Applications for Electronics and Optoelectronics*, 41.

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

WHERE INNOVATION BEGINS

ADDENDUM:

Novel In-situ Patterning Technique to Fabricate Single Quantum Dots for Quantum Photonics (222478)

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Team: John Klem (5266), Samuel Hawkins (5266), Alexander Hendrickson (5266), Julia Deitz (1819)
PM: Ryan Wixom (1881)

Purpose, Approach, and Goal

Motivation: Realizing high-quality, tunable **single-photon sources (SPS)**

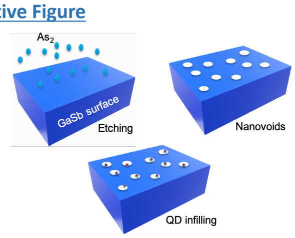
State-of-the-art: Solid-state SPS (e.g. semiconductor QDs) offer high efficiencies but are **limited by material choice and randomness in size/position**.

Hypothesis: QDs grown in **well-defined pattern** (aids uniformity) and with a **wide variety of materials** (tunable emission wavelength)

R&D approach:
1. Arsenic-assisted etch of III-Sb surfaces (Nanovoid pattern)
2. In-filling of void to form QDs

***One* key goal:** **Nanostructure formation** using above-mentioned R&D approach

Representative Figure

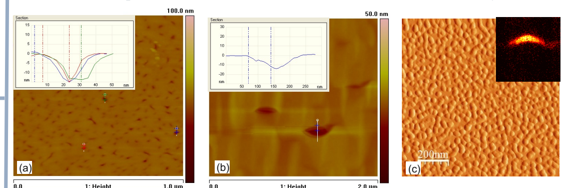


Schematic showing nanovoid formation on III-Sb surface by arsenic exposure followed by QD in-filling

Key R&D Results and Significance

R&D: Comprehensive study carried out to optimize experimental conditions: structure, growth temperature and As_2 exposure (time and flux).

- **Nanovoid formation + in-filled QD** realized – figure (a) and (b) below show AFM profile scans. These voids+QDs were found to have LOW uniformity
- **Ga(As)Sb QD** formation achieved without etch+infill process – figure (c) shows AFM and GaAs component TEM image (inset) of QDs. Novel technique to form etch-assisted QDs with efficient size, density control.

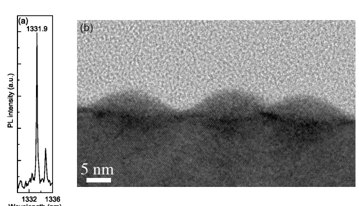


***One* key goal:** Nanostructure formation observed on structural measurements with both approaches; optical properties still need to be verified.

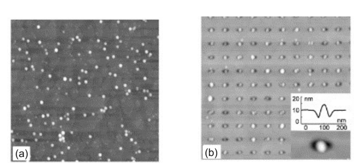
Follow-on plans and impact: 1. Full LDRD proposal for a device-level idea
2. Results (with optical properties) may be relevant to other QIS programs
3. Users plan to integrate QDs in cavities, metasurfaces etc. (CINT user program)

Publications, IP and staff development: 3 early career staff/postdocs part of the team (Addamane, Dietz and Hendrickson). Publication (APL), conference presentation (EMC 2022) and Technical Advance are planned.

Motivation : Single-photon source (SPS)



(a) PL spectrum and (b) TEM cross-section from InAs/GaAs QDs



Growth of InAs QDs on (a) unpatterned and (b) patterned substrate (ex-situ)

- SPS: key component of quantum information systems
- **State-of-the-art**: Semiconductor QDs offer high efficiencies & ease of integration. E.g. InAs QDs
- Drawbacks:
  - Self-assembly process – introduces randomness
  - Limited emission λ
- **Alternative**: Grow QDs in well-defined patterns
  - Reduce randomness
  - No material-choice constraints
- In-situ etching is better than ex-situ: avoids contamination and interface issues
- Current practice: Etching nanoholes using Ga, Al droplets and in-filling voids.

Zhou et al. Scientific reports, 4(1) 2014.

Kiravittaya et al. Physica E, 23(3-4) 2004.

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

WHERE INNOVATION BEGINS

Methods: Arsenic-assisted etch

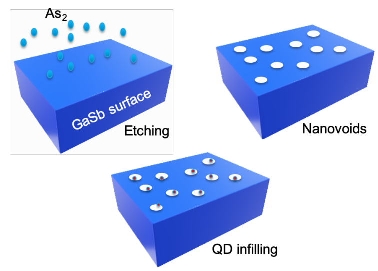
➢ **Approach:**

Use arsenic-induced etching on antimonide surfaces to form nanovoids and in-fill QDs

- Advantages:
  - In-situ etching process
  - No metal droplets used for etching
  - QD-infilling offers material flexibility

➢ **Go/no-go**:

- Milestone 1: Nanovoid formation
- Milestone 2: QD infilling



Growth process for realizing As-etched QDs on Sb surfaces

Anion exchange:

$$2GaSb + As_2 \rightarrow 2GaAs + Sb_2 \quad \Delta H^0 = -47.6\ kJ/mol$$

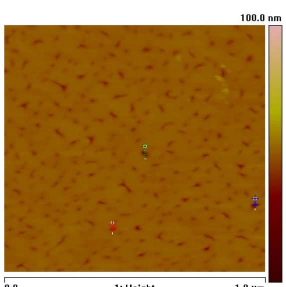
Isoelectronic AsSb formation

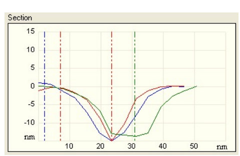
$$GaSb + As_2 \rightarrow 2GaAs + AsSb \quad \Delta H^0 = -33.9\ kJ/mol$$

As_2 reacts aggressively with GaSb in both cases

Losurdo et al. Journal of Applied Physics, 100(1) 2006.

Nanovoid & QD-infilling

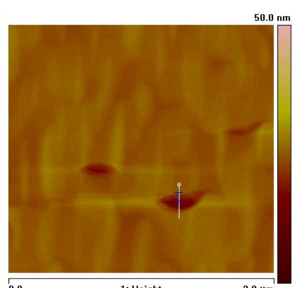


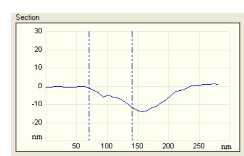


Vertical distances (nm):

- 16.58
- 15.21
- 13.72

AFM image of nanovoid surface with sectional analysis





- Depth: ~15nm
- QD height: 7-8nm

AFM image of in-filled nanovoid with sectional analysis

➢ **Success Metric**: Nanovoid formation

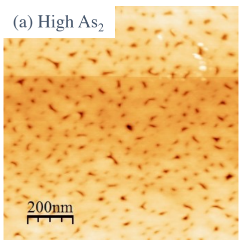
➢ **Success Metric**: QD in-filling

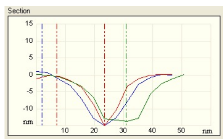
➢ Growth conditions can be tuned to adjust density, depth etc.

➢ Size/shape uniformity is LOW: issue for realizing efficient emission

➢ In-depth study carried out to improve uniformity

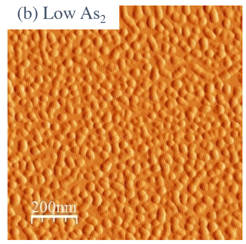
Nanovoid vs "QD" formation

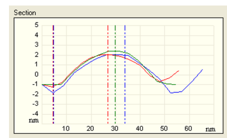




Nanovoid dimensions:

- Width : ~40nm
- Height : ~15nm





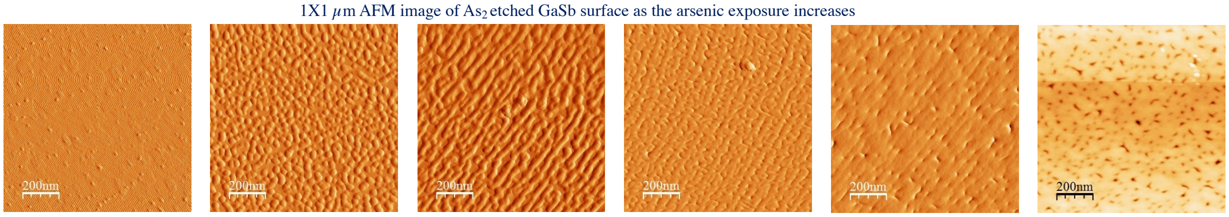
"QD" dimensions:

- Width : ~25nm
- Height : ~3nm

1X1 μm AFM image of (a) high and (b) low As_2 (flux and time) etched GaSb surface

- ➢ Etching mechanism heavily dependent on As_2 flux and exposure time – High As_2 → Nanovoids ; Low As_2 → "QDs"

1X1 μm AFM image of As_2 etched GaSb surface as the arsenic exposure increases

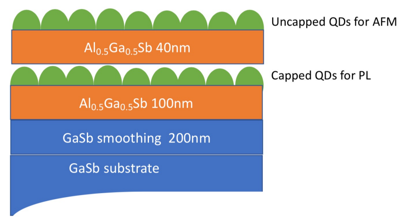


As_2 etched QDs

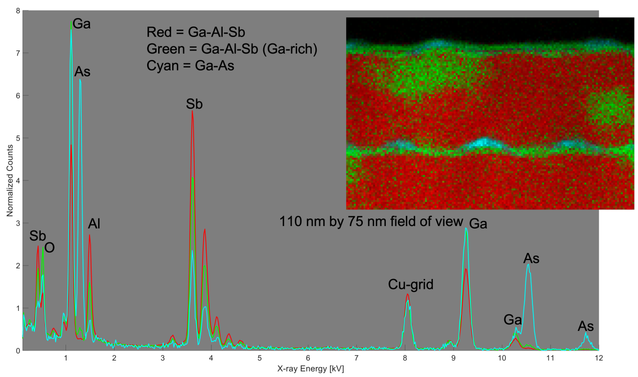
- QDs embedded in $Al_{0.5}Ga_{0.5}Sb$ barriers

  - higher bandgap for PL and contrast for TEM

- Material composition of QDs: Ga(Sb)As with a thin GaSb layer underneath



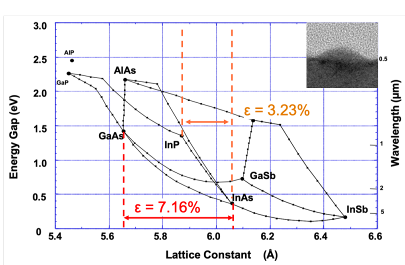
Structure for embedded As_2-etched QDs

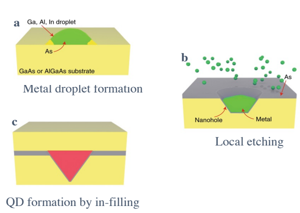


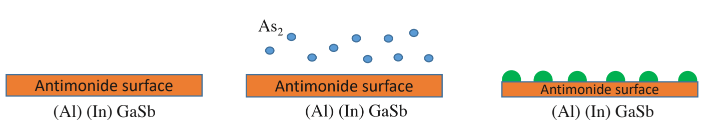
EDS analysis of As_2 etched QDs

Cross-sectional TEM image of As_2-etched QDs

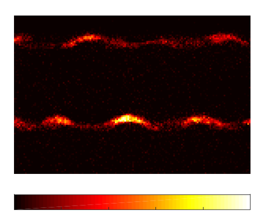
Why do we care?



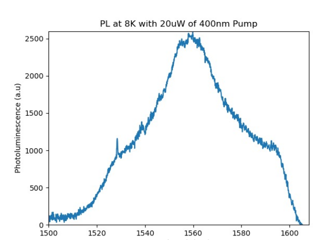




Comparison of existing methods to technique developed here



GaAs component TEM



Preliminary PL results

Gurioli et al. Nature Materials, 18(8) 2019.

LABORATORY DIRECTED RESEARCH & DEVELOPMENT
WHERE INNOVATION BEGINS

LDRD Project Metrics

Presentations and Publications

- Manuscript: " III-Sb nanostructures formed by arsenic-assisted surface etching" – to be submitted to Applied Physics Letters
- Presentation: Abstract to be submitted to Electronics Materials Conference (EMC) 2022 (due January 2022)

Intellectual Property

- Planned submission to technical advance: Novel technique to realize III-V nanostructures through surface etching

Tools and Capabilities

- III-V nanostructure growth added as a capability to the CINT user program.
  - Users: University of Maryland (UMD), National Institute of Standards and Technology (NIST)

Staff Development

- Early career staff/postdocs supported:
  - Sadhvikas Addamane (PI) – transitioned to staff Sept. 2021
  - Julia Deitz –TEM characterization
  - Alexander Hendrickson – MBE growth

Project Legacy

Key Technical Accomplishment

- Nanovoid formation and QD-infilling realized
- Developed arsenic-assisted nanostructure growth technique

Engagement with Sandia mission:

- Results (with optical characterization) may be relevant to other quantum information systems (QIS) programs at Sandia.

Plans for follow-on and partnerships:

- Full LDRD idea to be proposed on a device-based study integrated with As_2-etched QDs
  - Potential IAs: NMRF, MS or NI
- User interest in embedded QDs for multiple applications – may lead to joint proposals with external parties

What could have been done but didn't happen

- Extensive optical characterization to deduce/confirm dimensionality of nanostructures.