

Epitaxial Quantum Dot Infrared Photodetectors: From the Doping Conundrum to a New Paradigm of Surface/Interface Engineering

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Abstract. For epitaxial InAs/GaAs quantum dot infrared photodetectors (QDIPs), the central impediment to high-temperature operation above 150 K lies in the n-type doping step. Necessary though this doping is for generating an adequate photocarrier population, it simultaneously introduces deep-level defects, including DX centers, which in turn drive a sharp increase in dark current. Traditional optimization routes built around band-structure engineering are, at this stage, nearing their practical limits. Against that backdrop, the present review argues that a more foundational route may lie in borrowing the already mature surface chemical passivation strategies developed for colloidal quantum dots and translating their governing principles to epitaxial platforms. At atomic-scale resolution, surface and interface engineering of quantum dots can suppress defect-assisted tunneling and, just as critically, recover a large carrier escape activation energy. A stepwise examination is therefore undertaken: first, the physical origin of the doping-induced performance bottleneck is dissected; next, the contributions and constraints of established approaches, including dot-in-a-well (DWELL) architectures, are reviewed; and finally, the scientific rationale underlying this emerging surface/interface engineering paradigm is set out in detail. From that basis, future research directions are sketched prospectively, including the co-optimization of material growth, doping, and surface treatment, together with the exploration of hybrid-dimensional heterostructures, so as to furnish a systematic research framework for breaking through the QDIP performance bottleneck.

Keywords: quantum-dot infrared photodetectors (QDIPs), epitaxial quantum dots, so-called doping paradox, surface-level engineering, interface-directed engineering, InAs/GaAs heterostructures, elevated-temperature operation.

1. Introduction

Across national security applications, environmental monitoring platforms, and industrial sensing workflows, infrared photodetectors occupy a central position. Even so, broad deployment remains constrained by dependence on bulky, energy-intensive cryogenic cooling hardware. The field-defining objective, then, is the development of detectors that sustain high-performance operation at elevated temperatures (≥ 150 K), thereby opening a path toward compact, lower-cost systems [1].

Epitaxial quantum dot infrared photodetectors (QDIPs) remain a credible candidate for addressing this challenge. Owing to the three-dimensional quantum confinement inherent to QDs, several theoretical advantages arise: a discrete density of states, for one, is expected to suppress dark current and extend carrier lifetimes, thereby creating a plausible route toward efficient high-temperature operation [1]. Under device-realistic conditions, however, performance is sharply constrained by a fundamental "doping paradox" [2]. Although n-type doping is required to supply carriers for intersubband absorption, the same step also introduces deep-level defects (DX centers, for example). Dark current is then elevated dramatically, and, as a result, most high-performance QDIPs remain restricted to liquid-nitrogen temperatures.

The field now stands at an inflection point. Traditional optimization through band-structure engineering—dot-in-a-well architectures being the standard example—yields progressively smaller gains because it operates within, rather than rectifies, a doped material platform that remains intrinsically defect-prone [2, 3]. Running in parallel, the colloidal quantum dot (CQD) literature has made something quite clear: decisive optoelectronic advances have come not from ever more stringent bulk-purity targets, but from control at surfaces and interfaces (that, in practice, has been the real lever) [4]. Taken together, the analogy is hard to ignore; it indicates that an analogous shift in emphasis—one that treats atomic-scale surface and interface engineering as a central design rule rather than a secondary adjustment—may open a route to the high-temperature operation of epitaxial QDIPs.

Accordingly, this review advances the case for a necessary shift in paradigm. A systematic deconstruction is offered of the physical mechanisms underlying the doping bottleneck; lessons emerging from CQD surface science are examined critically; and concrete pathways, together with the attendant challenges, are delineated for implementing surface and interface engineering within epitaxial systems. At its broadest level, the analysis puts forward a coherent framework for the future co-design of materials, doping strategies, and interfaces, with the express aim of overcoming a longstanding performance barrier and enabling practical high-temperature QDIPs.

2. Physical roots of the doping paradox

For a credible assessment of what surface engineering can actually change, the exact physical route through which doping undermines QDIP performance has to be specified rather than assumed. The present section, accordingly, turns to the origin of doping-induced defects and the downstream penalties they impose, while also clarifying why conventional mitigation approaches remain intrinsically constrained.

2.1. Operational principle and the necessity of doping

At the level of device physics, a QDIP operates by photoexciting carriers—most often electrons—from a bound quantum-dot state (in most cases, the ground state) into a continuum or quasi-continuum state, after which the applied electric field sweeps those carriers out, thereby producing photocurrent. Within the extensively investigated InAs/GaAs materials platform, such operation requires that the QD ground states be populated with electrons at the outset. During molecular beam epitaxy (MBE) growth, this initial occupancy is ordinarily established through deliberate n-type doping, most commonly with silicon (Si), the usual target being roughly 1-2 electrons per dot so as to maximize intersubband absorption [2]. Functioning devices therefore cannot dispense with this doping requirement; therein lies the basic tension that defines the doping paradox.

2.2. Dopants as defect precursors: the DX center problem

Seminal studies in this area have made clear that Si dopants, far from constituting benign incorporations within the GaAs barrier matrix enveloping the InAs dots, actively perturb that host material [2]. In GaAs, silicon may assume multiple charge states and structural configurations. Particularly deleterious is one such configuration: the deep-level, metastable defect complex generally termed the DX center. Here, the donor atom occupies a distorted lattice arrangement accompanied by pronounced lattice relaxation, with the result that its bandgap energy level can shift substantially as its charge state changes [5]. Of still greater consequence, once ionization occurs, the positively charged Si donor together with the corresponding negatively charged DX-center configuration may generate a strong, spatially localized dipole moment [2, 6].

2.3. Nanoscale potential disorder and defect-assisted tunneling

For the device physics at issue, this nanoscale dipole field is not a minor perturbation; it is catastrophic. Across the electrostatic potential landscape originally meant to confine electrons inside the quantum dot, a pronounced and highly localized distortion is introduced. No longer does the confinement barrier retain the clean, sharply defined profile set exclusively by the InAs/GaAs heterojunction band offsets; instead, it is shot through with localized dips and peaks in potential, their origin traceable to these randomly distributed, doping-related dipoles. Within such a disordered potential landscape, efficient low-energy escape routes become available to electrons in the quantum dot, specifically through trap-assisted or defect-assisted tunneling (that is the operative leakage channel here, rather than the idealized one). Relative to classical thermionic emission over the original confinement barrier, this tunneling process demands substantially less activation energy.

2.4. Experimental manifestation: collapse of activation energy

The direct experimental signature of this effect is a dramatic reduction in the measured apparent activation energy (E_a) for dark current. In an ideal, defect-free QD, E_a should correspond approximately to the energy difference between the QD ground state and the conduction band edge of the barrier material, typically in the range of 150-200meV for InAs/GaAs systems. In practice, for doped InAs/GaAs QDIPs, E_a is often found to be suppressed to values around or below 100meV [2]. Given the exponential dependence of dark current density on activation energy, as governed by the Arrhenius relation $J_{dark} \propto T^{3/2} e^{-\frac{E_a}{k_B T}}$, even a modest reduction of 50meV can lead to an increase in dark current by several orders of magnitude at a fixed temperature. This collapse of E_a explains why doped QDIPs exhibit disappointingly high dark currents, compelling operation at cryogenic temperatures (e.g., 77 K) to suppress this noise source to acceptable levels, thereby nullifying the high-temperature advantage.

2.5. Inherent limitation of band engineering strategies

For years, the field's default response to this challenge has taken the form of increasingly sophisticated band-structure engineering. Arguably the clearest—and most technically successful—instantiation has been the dot-in-a-well (DWELL) architecture, in which InAs quantum dots are embedded not in pure GaAs, but instead within an InGaAs quantum well [3]. Several practical advantages follow from this configuration: partial relaxation of the compressive strain; wider tunability of the absorption wavelength through adjustment of the well composition; and an altered

effective confinement-potential profile that can, depending on the specific design window, improve carrier capture or extraction probabilities. Yet, despite the measurable performance gains associated with DWELL structures and related variants (including technologically important demonstrations such as multi-spectral detection), these designs remain, at bottom, optimizations within a flawed paradigm. What they do not do—this is the crux of the matter—is eliminate DX centers or other doping-induced defects. Instead, the band structure is engineered so that their detrimental effects are moderated to some extent, not removed. Against that backdrop, the fundamental operating-temperature ceiling imposed by the doping paradox, together with the accompanying defect-assisted tunneling pathway, remains largely unchanged. Read another way, the field's persistent dependence on such strategies suggests the need for a more radical reformulation of the problem: one that targets the defect mechanism at its source rather than continuing to manage its downstream symptoms.

3. Paradigm evolution: surface/interface engineering in colloidal quantum dots

As the epitaxial QDIP community continued to contend with limitations introduced by doping, a separate—though conceptually adjacent—research stream centered on colloidal quantum dots (CQDs) was advancing by way of a markedly different design logic. In applications such as high-color-purity displays (QLEDs) and solution-processed photovoltaics, the rapid ascent of CQDs did not emerge from any effort to approximate ideal, bulk-like crystal quality through the use of ultrapure precursors. Rather, as detailed with particular clarity in the landmark review literature, the field's central achievement lay in demonstrating that surface and interface chemistry—not precursor purity as such—could function as the dominant lever governing device performance [4]. Read against that trajectory, the development of CQD technology offers a compelling blueprint for what may amount to a broader paradigm shift in epitaxial optoelectronics.

3.1. The surface as the determining factor

At the level of atomic-scale surface termination, the performance of colloidal quantum dots proves acutely sensitive. In early-generation CQDs, long-chain insulating organic ligands—oleic acid and oleylamine being the standard examples—were used during synthesis, yet that formulation brought with it two study-defining liabilities: first, inter-dot charge transport was rendered exceedingly inefficient because carriers faced an insulating ligand barrier; second, under-coordinated surface atoms (that is, dangling bonds) generated a high areal density of surface trap states. Those trap states, in turn, functioned as highly efficient non-radiative recombination centers, with photoluminescence quantum yield (PLQY) and overall device efficiency both being sharply constrained.

3.2. Ligand engineering: from insulating shells to conductive bridges

A first study-defining shift in the field emerged with the advent of surface ligand exchange methodologies. By substituting bulky, electrically insulating organic ligands with compact inorganic species, researchers realized two tightly linked objectives at once: (i) effective passivation of electronic trap states through covalent saturation of dangling bonds, and (ii) a pronounced increase in electronic coupling among adjacent dots. Particularly effective in this regard were metal halides, including lead iodide (PbI_2) and zinc iodide (ZnI_2), which functioned as passivating ligands [7]. Bound directly to the QD surface, these species could "heal" mid-gap states (that is, suppress the defect-related states responsible for nonradiative loss pathways), yielding PLQYs that often

approached 100%. Just as importantly, their small steric footprint and ionic character facilitated efficient charge transport, with the result that CQD solids exhibited carrier mobilities several orders of magnitude higher than those of their organic-ligand-capped predecessors [4]. What this transition altered, in practical as well as conceptual terms, was the status of ligands themselves: no longer treated as mere steric stabilizers, they came to be regarded as active constituents of the electronic structure.

3.3. Advanced nanostructure engineering: core-shell and graded interfaces

Moving well past straightforward ligand exchange, increasingly elaborate colloidal synthetic routes were devised to impose atomic-scale control over the full potential landscape encountered by charge carriers. By growing a wider-bandgap semiconductor shell (for example, CdS or ZnS) around a core quantum dot (such as CdSe), thereby forming a core-shell heterostructure, spatial separation of electrons and holes could be established; wavefunction overlap was correspondingly reduced, and non-radiative Auger recombination was therefore suppressed—a study-defining bottleneck in high-brightness LED operation and optical-gain applications. Pushing the architecture further, gradient-alloyed shells and "giant" core-shell structures with thick shells introduced a smooth, compositionally graded potential barrier. Under those design conditions, Auger processes were suppressed more effectively, resistance to photo-oxidation was improved, and finer control over charge-carrier dynamics became achievable [4].

3.4. The translational insight for epitaxial qdips

What the CQD literature has made plain is this: the electronic and optoelectronic behavior of a semiconductor nanostructure is governed not only by its intrinsic bulk band structure, but equally—indeed, in many cases more strongly—by the chemistry and physics localized at its surfaces and interfaces. Within colloidal systems, surface engineering functions as the principal lever for performance tuning, marking a distinct shift in emphasis away from "bulk properties achieved through growth and doping" and toward "interface properties achieved through synthetic and processing chemistry."

When this line of reasoning is carried over to epitaxial InAs/GaAs QDs, a powerful—though still largely uncharted—route toward innovation comes into view. Formed through the Stranski-Krastanov growth mode and later encapsulated by GaAs, the surfaces of epitaxial QDs remain interfacial regions with a high density of unsaturated bonds. More specifically, the doping-induced DX centers, although located within the barrier, are tightly coupled to the local chemical and electrostatic conditions at and near the QD/barrier interface. A study-defining question follows from that linkage: might a post-growth or in-situ surface treatment, conceptually borrowed from CQD chemistry, passivate not only the QD surface states but also neutralize, or at least electronically isolate, the detrimental DX centers? In theoretical terms, should a deliberately engineered interfacial layer be able to screen the local dipole fields generated by DX centers or alter the Fermi-level pinning at the interface, the intended confinement-potential profile could be re-established. That single shift matters. By raising the effective carrier-escape activation energy from a defect-pinned value of approximately 100 meV back toward the intrinsic approximately 150-200 meV range, the Arrhenius relationship implies a reduction in dark current at 150 K by roughly one to two orders of magnitude. At the device level, such an improvement could mark the difference between QDIPs remaining laboratory curiosities that require liquid-nitrogen cooling and becoming practical platforms operable with compact thermoelectric coolers.

4. Pathways and challenges for surface/interface engineering in epitaxial QDIPs

Reconciling the solution-phase chemistry of QDs with the ultra-high-vacuum, high-temperature conditions characteristic of epitaxial growth constitutes a demanding—yet unavoidable—interdisciplinary problem. What is required, at bottom, is the coupling of atomic-scale chemical tunability with the process-level exactitude of epitaxial fabrication. From this standpoint, several technical routes, not mutually exclusive, come into view; each offers distinct possibilities while also introducing substantial obstacles, and together these routes delineate the research agenda for this still-emerging paradigm.

4.1. Pathway I: post-epitaxy wet-chemical and vapor-phase functionalization

This approach represents the most direct analog to QD processing, applying passivation treatments after the complete epitaxial growth of the QDIP heterostructure.

Such approaches may take the form of *ex situ* solution-phase immersion in passivating media (for example, solutions containing metal halides, chalcogenides such as $(\text{NH}_4)_2\text{S}$, or selected organic thiols) or, alternatively, vapor-phase routes such as atomic layer deposition (ALD). Particularly attractive is ALD: with monolayer-level control and notably strong conformality, it can, in principle, facilitate the deposition of ultrathin and spatially uniform metal-oxide films (e.g., Al_2O_3 , ZnO) or chalcogenide layers across exposed surfaces.

Chemical compatibility, together with interfacial stability, constitutes the principal constraint. Reagents must establish stable, electrically benign bonding configurations with GaAs and InAs surfaces, yet do so without driving additional oxidation or generating new interface states, which could then function as recombination centers or carrier-scattering sites. In the ALD context, the starting surface chemistry matters acutely, as does the thermal stability of the deposited layer under actual device-operating conditions. By the same token, any passivating layer must survive the subsequently imposed, often harsh, fabrication sequence—plasma etching, high-temperature annealing, and metallization included. Added to this, and not trivially, is the difficulty of achieving uniform penetration to, and modification of, the buried QD/barrier interface when access is attempted only from the top surface.

4.2. Pathway II: in-situ surface modification during epitaxial growth

A more integrated route entails *in situ* modification of the QD surface inside the MBE or metal-organic chemical vapor deposition (MOCVD) chamber, a shift that offers, at least in principle, cleaner and more tightly controlled interfaces.

This could be accomplished by halting controlled growth immediately following QD formation, yet prior to deposition of the capping barrier layer. At that juncture, the introduction of a calibrated flux of a reactive species—atomic hydrogen, nitrogen, sulfur, or alternatively a metal-organic precursor—could enable a self-limiting surface reaction specifically configured to terminate dangling bonds in a controlled manner (that surface-chemistry timing is the operative point here, not merely the species choice). As one concrete example, a tightly regulated exposure to an As_2 beam under optimized conditions might shift the As:Ga stoichiometry at the dot surface, thereby reducing trap states associated with group-III vacancies.

At issue, above all, is the attainment of exacting kinetic and thermodynamic control. Across the wafer, the modification step must proceed with high spatial uniformity and, from run to run, with equally tight reproducibility. Just as critically, no undesirable morphological perturbation can be

introduced into the sensitive QDs—no decomposition, no ripening, no alloying—as any such change would shift the size distribution and, with it, the electronic properties. What this ultimately demands is a fundamental, process-level understanding of the surface reconstruction dynamics of InAs and GaAs under differing beam-equivalent pressures and substrate temperatures.

4.3. Pathway III: interface design via low-dimensional and hybrid heterostructures

What this pathway requires is a more architecture-level reconceptualization of the QDIP itself, such that novel material systems are developed in which the relevant interfaces are either easier to engineer or, by their very makeup, already exhibit advantageous properties.

Conceptually, much may be gained by drawing on advances in low-dimensional systems. In one illustrative case, crystal-phase quantum dots grown within III-V semiconductor nanowires provide a platform marked by a sharply elevated surface-to-volume ratio and, given their facet-specific chemistry, potentially altered interfacial reactivity that may render them especially susceptible to surface treatment protocols [8]. Pushing the idea further, one can also envisage hybrid epitaxial-colloidal architectures in which an epitaxially grown QD array is subsequently functionalized with a precisely assembled monolayer composed of designed colloidal nanoparticles or molecular species. At another emerging boundary, epitaxial QD layers may be integrated with two-dimensional materials—graphene and transition metal dichalcogenides such as MoS₂ being obvious examples—or with wide-bandgap semiconductors, including AlN and ZnO, to serve as charge-transport or confinement layers.

In the present context, the central difficulties arise from heterogeneous integration and, no less importantly, from the need for new characterization approaches. When disparate material platforms are brought together—for instance, epitaxial III-V compounds with 2D materials or with solution-processed layers—there emerge intricate interfacial chemistries, lattice-mismatch constraints, and incompatibilities in thermal budget (a recurring bottleneck in mixed-platform device stacks). For nanowire-embedded QDs, fabrication routes and electrical contacting are rendered more difficult. Equally, across these complex and frequently non-planar geometries, probing electronic properties and assessing interfacial quality calls for the development of analytical techniques not yet standard in the field.

4.4. Overarching scientific and technological hurdles

Beyond the challenges specific to each pathway, several overarching hurdles must be cleared for any surface engineering approach to succeed.

A major obstacle lies in the absence of standardized, high-sensitivity methods capable of directly interrogating the chemical and electronic character of the buried QD/barrier interface within a fully realized device heterostructure. Within that constraint, linking any given surface treatment to a quantitative shift in DX center concentration or configurational state becomes analytically formidable. To establish processing-structure-property relationships, advanced approaches—cross-sectional scanning tunneling microscopy (X-STM), atom probe tomography (APT), and carefully structured in-operando photocurrent and impedance spectroscopy measurements—will be indispensable.

Operational stability is equally decisive. Under bona fide QDIP operating conditions—elevated temperature and an applied bias, not merely ambient benchtop exposure—any candidate passivation strategy must exhibit sustained thermal, chemical, and electrical stability over extended periods. For

technological viability, just as critically, that strategy must remain compatible with standard high-yield device-fabrication workflows.

The overriding objective is a lower dark current, but not at the expense of photocurrent, with the optical response kept intact. To that end, no surface treatment can be allowed to erode the two study-defining optical parameters: the intersubband absorption coefficient (set by wavefunction overlap and the doping profile) and the intrinsic carrier lifetime within the dots. What is required, then, is an improvement that is truly holistic.

Any surface-engineering strategy is, in the end, judged by what it does to the device figure of merit: detectivity (D), the metric that sets responsivity (that is, signal) against noise current, including dark current and its attendant fluctuations. Across these tightly coupled constraints, validation of this emerging paradigm will require a coordinated, genuinely multidisciplinary push, one directed at the full set of interdependent challenges rather than any single parameter in isolation.

5. Conclusion and integrated outlook

The development of epitaxial QDIPs remains bounded by the field's underlying "doping paradox." Although band-structure engineering has produced measurable—if largely incremental—gains, such tuning does not remove the defect populations introduced by doping itself; those defects, in turn, depress the carrier escape activation energy (E_a) and drive dark current upward. Against that material constraint, the present review contends that a genuine shift in design logic is required. Drawing explicitly on the transformative precedent of surface and interface engineering in colloidal quantum dot technologies, it proposes that atomic-scale surface control be treated not as a secondary optimization step, but as a design principle fully co-equal with growth and doping.

This emerging paradigm gestures toward a future centered on holistic co-design. Among the most immediate research frontiers are the following: a first-principles interrogation of passivation mechanisms so that their interactions with defect states (including DX centers) can be resolved more cleanly; the co-optimization of surface treatments with advanced growth strategies, such as droplet epitaxy [9], alongside doping schemes such as δ -doping, where genuinely synergistic effects may arise; and the exploration of device architectures made possible by deliberately engineered interfaces, including QD-2D material heterostructures. For that broader vision to be realized, collaboration on an unusually tight scale—across materials science, chemistry, and device engineering—will be required.

By looking past the long-standing doping bottleneck through deliberately targeted surface and interface engineering, the field may at last realize the much-invoked objective of high-performance infrared photodetectors that remain effective at elevated operating temperatures, thereby opening a new phase in infrared technology.

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