# 学 位 論 文 内 容 の 要 旨

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## 学 位 論 文 題 名

Metal-Hydride-free Colloidal Synthesis of $InP_{1-x}Sb_x$ Quantum Dots Using Aminophosphine for Optoelectronic Applications
（オプトエレクトロニクス素子創製へ向けた $InP_{1-x}Sb_x$ 量子ドットのアミノホスフィンを用いた金属水素化物フリーコロイド合成）

Quantum dots (QDs) are ultrasmall semiconductor nanocrystals that exhibit pronounced quantum confinement effects. In 2023, Alexei Ekimov, Louis Brus, and Moungi Bawendi were awarded the Nobel Prize in Chemistry for their pioneering contributions to the discovery, understanding, and controlled synthesis of QDs.

In them, NIR-SWIR emitting QDs have emerged as a highly versatile class of materials, bridging fundamental photo-physics and a wide range of practical applications. Their size-tunable bandgaps, narrow emission linewidths, and high absorption coefficients make them particularly attractive for optoelectronic and biomedical technologies.

However, most state-of-the-art NIR–SWIR QDs are based on Pb and Hg chalcogenides, whose intrinsic toxicity and stringent RoHS restrictions severely limit their commercial translation. This creates an urgent need to develop environmentally benign, RoHS-compliant alternatives. In this context, InSb stands out as a highly promising candidate. As the III–V semiconductor with the narrowest bulk bandgap, the largest exciton Bohr radius, and one of the highest carrier mobilities, InSb offers exceptional potential for NIR–SWIR emission. Moreover, unlike many III–V compounds, InSb contains no arsenic, resulting in significantly lower toxicity while maintaining excellent infrared optoelectronic properties. These intrinsic advantages position InSb QDs as an attractive next-generation platform for infrared imaging, detection, display, and photonic technologies.

However, the reported synthetic routes for InSb QDs remain limited, with only a narrow selection of viable precursors and reaction chemistries. As a consequence, the optical performance of existing InSb QDs—particularly their photoluminescence efficiency—still falls far short of what is required for practical NIR–SWIR applications. In this work, we employ aminophosphine as a low-reactivity reducing agent to synthesize InSb QDs as well as $InP_{1-x}Sb_x$ alloyed QDs, and we analyze the underlying reaction mechanisms in detail. Furthermore, we successfully prepare InSb/InP core–shell QDs to improve surface passivation and spectral stability, and we integrate these materials into QLED devices to demonstrate their potential for infrared optoelectronics.

In Chapter 1, we introduced the fundamental physical aspects of QDs, including quantum confinement effects, their characteristic optical properties, and the origin of the Stokes shift. On the chemical side, we summarized the two major synthetic strategies used in colloidal QD chemistry—namely, the hot-injection method and the heat-up method—highlighting their respective advantages and limitations. For NIR–SWIR emitting QDs, we outlined the main application fields and provided a brief overview of their material classes and current research progress. Finally, we articulated the motivation of this study, emphasizing the need for RoHS-compliant III–V alternatives and the potential of InSb-based QDs for next-generation infrared optoelectronic technologies.

In Chapter 2, we reviewed the existing precursor systems and synthetic approaches for InSb QDs. The precursors currently used for InSb synthesis can be categorized into three components: the indium precursor, the antimony precursor, and the reducing agent. Notably, all reported reducing agents to date are metal-hydride–based strong reductants, with Super-Hydride being the most widely employed. Such strong reducing agents are capable of overcoming the intrinsic difference in reduction potentials between In and Sb precursors, enabling their simultaneous and stoichiometric reduction to metallic In and metallic Sb, which subsequently react to form metal-impurity-free InSb QDs. However, the excessively high reduction rate of strong hydrides introduces safety concerns and significantly limits its reaction controllability. Developing a synthesis route based on a mild reducing agent is therefore

highly desirable. In this thesis, we employed aminophosphine as a weak reducing agent and achieved the synthesis of impurity-free InSb QDs by tuning the ratio of indium to antimony precursors and by using an Sb–OLA precursor. Mechanistic investigation revealed that, despite differences in reducing strength, the reaction pathway in the aminophosphine system mirrors that of strong hydride systems: the precursors are first reduced to metallic intermediates, which subsequently react to form InSb QDs. This demonstrates that a metal-hydride-free approach can successfully generate high-quality InSb QDs while offering improved safety and reaction controllability.

In Chapter 3, we optimized the reaction temperature and established that higher temperatures yield narrower QD bandgaps. By jointly considering the intensity of the excitonic absorption peak and the strength of PL emission, 250 ℃ was identified as the optimal reaction temperature for metal-hydride-free InSb CQD synthesis. We then compared samples synthesized with and without Zn addition and found that Zn markedly enhances the optical properties of InSb QDs, producing sharper excitonic features and significantly stronger PL emission. Finally, we examined the use of $InCl_3$ as an alternative indium precursor by partially substituting Indium carboxylate. Increasing the $InCl_3$ substitution ratio resulted in progressively narrower bandgaps but also led to weaker excitonic shoulders. TEM analysis revealed that higher $InCl_3$ fractions promote aggregation, with severe clustering observed at 50% substitution, where large nanoflower-like structures were formed. Although these clusters exhibit reduced bandgaps, their morphology is unsuitable for practical optoelectronic applications.

Within the family of III–V quantum dots, InAs is currently the only material system capable of spanning the combined bandgap range of InP and InSb. However, the severe inherent toxicity of arsenic greatly limits the applicability of InAs QDs in biological and other sensitive environments. As an alloy system bridging the bandgaps of InP and InSb, $InP_{1-x}Sb_x$ offers a promising RoHS-compliant alternative to InAs, providing continuous bandgap tunability across the NIR–SWIR region. In Chapter 4, we replaced the Sb–OLA precursor used in the previous chapters with an Sb–TOP precursor and successfully achieved, for the first time, the synthesis of $InP_{1-x}Sb_x$ alloy QDs. We further elucidated the reaction mechanism underlying alloy formation. Characterization of the Sb–TOP precursor by $^{31}P$ NMR and EXAFS revealed that it exists predominantly as a sterically hindered, four-coordinate complex $Sb[Cl(TOP)_3]^{2+}$. Due to its substantial steric bulk, this species resists reduction by aminophosphine, leaving a significant amount of unreacted aminophosphine in the reaction environment. The excess aminophosphine promotes side reactions that would otherwise be difficult to initiate, leading to the formation of InP units. These InP units subsequently merge with nascent InSb QDs, giving rise to the $InP_{1-x}Sb_x$ alloy phase. The relative incorporation of P and Sb in the alloy can be systematically tuned by adjusting the Sb/In feeding ratio, thereby enabling precise control over the resulting bandgap.

In Chapter 5, we employed aminophosphine simultaneously as the reducing agent for InSb and as the phosphorus precursor for InP shell growth, enabling the successful synthesis of InSb/InP core–shell QDs. The resulting core–shell structures exhibited significantly enhanced optical properties, including higher PLQY and narrower PL emission linewidths compared with bare InSb cores. Using these InSb/InP core–shell QDs, we fabricated, for the first time, an InSb-based QLED device and achieved electroluminescence in the NIR–SWIR region. This demonstration highlights the potential of metal-hydride-free InSb and its heterostructures for next-generation infrared optoelectronic applications.

Across this thesis, we developed a metal-hydride-free strategy for synthesizing InSb-based QDs and extended it to alloyed $InP_{1-x}Sb_x$ and InSb/InP core–shell QDs. We clarified precursor chemistry, established controllable reaction pathways, and optimized key parameters to improve crystallinity and optical performance. Mechanistic insights into aminophosphine reduction and Sb–TOP complexation. Finally, we demonstrated the first InSb-based QLEDs achieving NIR–SWIR electroluminescence. These results provide a safer, RoHS-compliant route to III–V infrared QDs and advance their applicability in next-generation optoelectronic technologies.