

Local Structure Analysis of Sb–TOP Precursors by Sb K-edge XAFS

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1 Introduction

III–V quantum dots (QDs) have attracted considerable attention for optoelectronic applications such as light-emitting and photodetecting devices owing to their high carrier mobility and composition-tunable bandgaps. Among them, InSb QDs are promising materials for short-wave infrared (SWIR) applications because of their excellent optical properties. However, the colloidal synthesis of InSb QDs generally requires strong metal hydride reducing agents, such as LiEt₃BH, which present challenges in terms of safety and reaction control. We have developed a metal-hydride-free synthetic route to InP_{1-x}Sb_x alloy QDs using tris(dimethylamino)phosphine [P(NMe₂)₃], an air-stable and mild reducing agent that also serves as a phosphorus source. In this method, a solution prepared by mixing SbCl₃ and trioctylphosphine (TOP) acts as an antimony precursor (Sb–TOP). Although the Sb–TOP precursor was found to play a crucial role in the formation of InP_{1-x}Sb_x alloy QDs, its local structure and coordination environment, and their impact on the reaction pathway, remained unclear. In this study, Sb K-edge X-ray absorption fine structure (XAFS) measurements were performed to elucidate the local structure of the Sb–TOP precursor. In particular, the coordination environment around Sb was investigated by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses, and its relationship to the formation mechanism of InP_{1-x}Sb_x alloy QDs was examined.

2 Experiment

To investigate the local structure of the Sb precursor, solutions containing SbCl₃ and trioctylphosphine (TOP) were prepared. SbCl₃ was dissolved in TOP, and samples with Sb/TOP molar ratios ranging from 1:3 to 1:20 were prepared. XAFS measurements were carried out at the AR-NW10A beamline of the Photon Factory Advanced Ring (PF-AR). Measurements were performed at the Sb K-edge (~30.5 keV) using monochromatic X-rays obtained with a Si(311) double-crystal monochromator. The SbCl₃–TOP

precursor solutions were loaded into liquid cells and measured in transmission mode. For energy calibration, a standard sample consisting of Sb₂O₃ mixed with BN was used, and the first inflection point of the Sb K-edge was set to 30492.0 eV. The obtained XAFS spectra were processed using Athena¹ included in the Demeter package for background subtraction and normalization. The k-space spectra were subsequently Fourier transformed to obtain radial structure functions. EXAFS fitting was performed using Artemis¹ to determine the coordination numbers and bond distances around the Sb atoms.

3 Results and Discussion

Figure 1 shows the Sb K-edge XANES spectra of SbCl₃ and the SbCl₃ = 1:3 precursor solution. The absorption edge positions of the two samples were nearly identical, indicating that the oxidation state of Sb was not significantly altered by the addition of TOP. This result suggests that Sb predominantly remains in the +III oxidation state even in the Sb–TOP precursor. In contrast, noticeable changes were observed in the white-line intensity and the oscillatory features at higher energies, implying that the coordination environment around Sb was modified by TOP coordination. Figure 2 shows the EXAFS oscillation spectra of crystalline SbCl₃ and the Sb–TOP precursor solution. Compared with crystalline SbCl₃, the Sb–TOP precursor exhibited a markedly reduced EXAFS oscillation amplitude, indicating increased structural disorder around the Sb atoms. This observation suggests that the well-defined crystalline coordination environment of SbCl₃ is transformed into a more flexible and disordered coordination structure in solution through coordination with TOP. Furthermore, the FT-EXAFS spectra shown in Figure 3 reveal that the Sb–Cl peak at approximately 2.1 Å, originating from crystalline SbCl₃, gradually decreased with increasing TOP concentration. In contrast, a new shoulder peak appeared at approximately 2.4 Å, and its intensity increased as the TOP concentration increased. This feature is attributed to Sb–P scattering, indicating the direct coordination of TOP to Sb. EXAFS fitting of the

$\text{SbCl}_3 = 1:3$ precursor solution yielded coordination numbers of 2.9 for Sb–P and 0.7 for Sb–Cl. The corresponding bond distances were determined to be 2.59 Å for Sb–P and 2.41 Å for Sb–Cl. These results indicate the presence of approximately three TOP molecules and less than one chloride ligand around each Sb atom, suggesting that SbCl_3 undergoes partial chloride dissociation in solution and forms a TOP-coordinated species. Based on the EXAFS analysis, the Sb–TOP precursor is proposed to possess a coordination structure similar to $[\text{SbCl}(\text{TOP})_3]^{2+}$.

As a preliminary experiment, the Sb–TOP precursor was heated at the same temperature used for the quantum dot synthesis, and the formation of Sb(0), which serves as a monomer species during growth, was confirmed. This

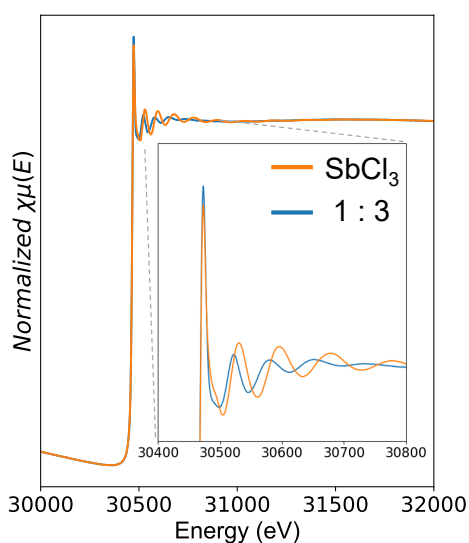


Figure 1. Sb K-edge XANES spectra of crystalline SbCl_3 and the $\text{SbCl}_3:\text{TOP} = 1:3$ precursor solution.

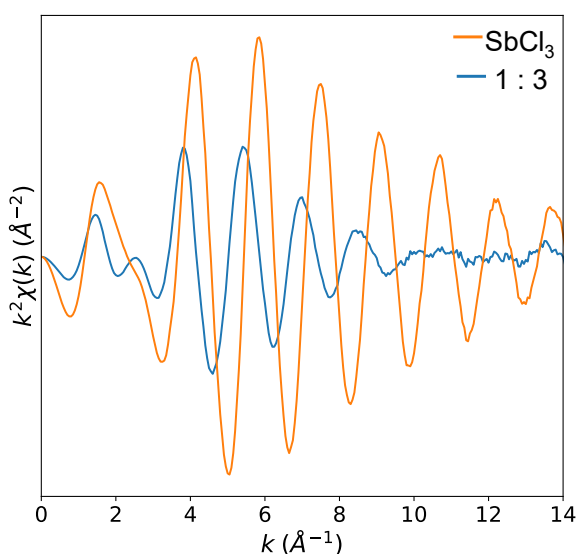


Figure 2. k^2 -weighted Sb K-edge EXAFS oscillation spectra of crystalline SbCl_3 and the $\text{SbCl}_3:\text{TOP} = 1:3$ precursor solution.

result suggests that TOP is oxidized during heating, accompanied by the reduction of Sb(+III) to Sb(0). Therefore, the proposed coordination structure is considered to be a highly reactive precursor that undergoes structural transformation under the reaction conditions. These findings indicate that the Sb–TOP precursor exhibits reactivity distinct from that of SbCl_3 alone, and that this unique reactivity plays an important role in the formation of $\text{InP}_{1-x}\text{Sb}_x$ QDs.

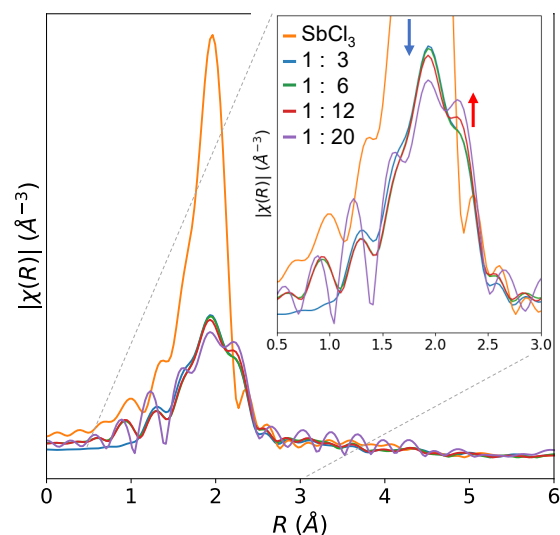


Figure 3. Fourier-transformed Sb K-edge EXAFS spectra of SbCl_3 and $\text{SbCl}_3:\text{TOP}$ precursor solutions with different Sb/TOP molar ratios.

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Research Achievements

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