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Growth and Characterization of Self-Assembled Quantum Dots for Intermediate Band Solar Cells

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Growth and Characterization of Self-Assembled Quantum Dots
for Intermediate Band Solar Cells

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Science
in Electrical Engineering

by

Meng Sun

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ABSTRACT OF THE THESIS

Growth and Characterization of Self-Assembled Quantum Dots for Intermediate Band Solar Cells

By
Meng Sun

Master of Science in Electrical Engineering
University of California, Los Angeles, 2013
Professor Diana Huffaker, Chair

In this study, Molecular Beam Epitaxy technology is presented in detail and several powerful characterization techniques such as XRD, AFM, TEM, PL are also reviewed. SAQDs are discussed to be applied in IBSCs application due to the formation of intermediate band which helps to absorb sub-band gap photons. We investigate how the structural and optical properties of InAs self-assembled quantum dots buried in AlAs$_{0.56}$Sb$_{0.44}$ barriers can be controlled through the use of thin GaAs$_{1-x}$Sb$_x$ cladding layers. Structural and optical properties of the SAQDs are studied, and the characteristics we demonstrate for this quantum dot system show great potential for application in intermediate band solar cells.
The thesis of Meng Sun is approved.

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2013
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1. Introduction

Solar energy is one of the most promising solutions for the current global energy problem. The maximum thermodynamic efficiency for the conversion of solar radiation into electrical energy was determined by Shockley and Queisser (S-Q) to be about 31% for a solar cell,\(^1\) operating under un-concentrated sunlight. Luque et al. proposed Intermediate band solar cell (IBSC) concept\(^2\) which is a solar cell with a single intermediate electronic band created by nanometer-sized semiconductor nanoparticles (quantum dots) inserted into the i-region of an ordinary p-i-n junction solar cell that could offer high conversion efficiency up to 63.2%. IBSCs benefit from high photocurrents generated due to the absorption of sub bandgap photons between the valence band (VB) and intermediate band (IB) and the intermediate band and conduction band (CB). Semiconductor quantum dots are the best choice to achieve intermediate band in a single junction solar cell due to their quantum confinement properties. In order to achieve the highest efficiency using IBSC, it is vital to study the concept on a suitable material system in a systematic approach. A proposed solution is to use a QD/barrier system of antimony based ternaries. In what follows, a review of molecular beam epitaxy technology is presented and several powerful characterization techniques such as XRD, AFM, TEM, and PL are also reviewed. Finally, the development of self-assembled quantum dots (SAQDs) material toward IBSCs is discussed.
2. Molecular Beam Epitaxy Overview

a. MBE Growth Overview

Molecular Beam Epitaxy (MBE) is a deposition process based on the interaction of beams of atoms and molecules on a heated substrate under ultra-high vacuum (UHV) conditions. There are different types of MBE systems, such as (1) Gas-Source MBE (GS-MBE) of III-V materials where hybrids like arsine (AsH$_3$) or phosphine (PH$_3$) are used as group-V materials, (2) Metalorganic MBE (MO-MBE) where trimethylindium (TMIn) and triethylgallium (TEGa) are used as group-III materials, (3) and Solid-Source MBE (SS-MBE) where high purity group-III and -V molecular materials are used to evaporate the source materials. Samples in this work are all grown with the SS-MBE system in the Integrated NanoMaterial Laboratory (INML) at UCLA (as shown in Fig. 1(a)). The UHV environment is required in the system to limit the contaminants doping from the background, a combination of mechanical pump, turbo pump, ion pump, and cryo pump are used to maintain the UHV condition at $10^{-8}$ – $10^{-11}$ Torr range in the whole system.

The sample substrate is held on a continuous azimuthal rotation (CAR) device at a sufficient temperature to activate the thermal migration of the depositing materials on the surface, the CAR device also rotates slowly during the growth in order to improve the uniformity of the epitaxial deposition. The fluxes of the materials are extremely important in the MBE growth, and need to be carefully calibrated. The material fluxes are mainly affected by the effusion cell temperatures, and are also controlled by mechanical
shutter and valve positions (for group V valved cracker cells). To monitor the pressures and fluxes of the materials, thermocouples and ion gauges are incorporated in the system.

MBE systems are also installed with a mass spectrometer to monitor the gas species in the vacuum chamber, a Reflection High Energy Electron Diffraction (RHEED) equipment to conduct in-situ analysis of the growth surface, and a pyrometer to keep track of the growth temperature. A typical MBE system is shown in Fig. 1(b).\textsuperscript{3} Besides the above mentioned components, other powerful characterization methods, such as Secondary Ion Mass Spectroscopy (SIMS), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) could also be installed onto the growth chamber to monitor the growth.

Fig. 1: (a) SS-MBE systems in the Integrated NanoMaterial Laboratory (INML) at UCLA (b) A schematic illustration of a typical MBE system equipped with effusion cells, CAR, ion gauge, cryoshrouds, RGA and RHEED gun/screen

b. RHEED Overview

RHEED is a very powerful characterization tool in the MBE system, it characterizes the surface reconstruction of the material. An electron gun at a voltage of 10-50kV is
used as a source of high energy electrons, the accelerated electrons hit the epitaxial surface at a very shallow angle, a scattered diffraction pattern would then be created on a fluorescent screen, and the surface information could be monitored. The allowed diffraction patterns can be predicted from the Ewald sphere, and due to the fact that the crystal perpendicular to the growth direction does not contribute to the RHEED pattern diffraction, thin smooth layers would show diffraction pattern as vertical rods on the RHEED screen. XRD cannot be used to probe the surface reconstruction because X-ray penetrates deep into the sample, as for the electron beam in RHEED, it doesn’t travel into the crystal and the shallow incident angle also minimizes sample penetration so that surface reconstruction can be characterized.

One of the applications of RHEED is to determine the growth rate of the deposition process using the RHEED oscillation method. This is a very powerful tool to calibrate growth rate before every growth, and helps to improve the accuracy of the growths. In RHEED oscillation measurement, the rotation of the CAR is stopped and the intensity of the diffraction spot is tracked as a function of time, the surface morphology changes between layers which gives rise to the oscillations, and useful information like growth rate could be extracted.
An example of RHEED oscillations measurement is shown in Fig. 2. At the beginning of the deposition, the flat surface constructs the zero order diffraction spot with high intensity. As the deposition proceeds, atoms arrive at the surface and start to form small islands on the surface to minimize surface energy, the intensity of the zero order diffraction spot begins to decrease because of beam scattering and surface imperfection. The intensity of the spot increases and reaches the next peak when a complete layer is formed. The intensity of peaks decreases as the growth continues due to the imperfections in layer by layer growth. After the deposition is stopped, the atoms begin to migrate on the surface to form a smooth surface and the intensity of the diffraction spot increases to the initial value. The time in one period is the time the deposition process needs to form one monolayer (ML), and the growth rate has the unit of ML/s. Using the lattice constant of the depositing material, the growth rate can be converted to nm/s or µm/h.

c. Self-assembled Epitaxial Nanostructures

A patterned substrate can be used to form epitaxial quantum dots (QDs). The spacing and pitch of the pattern could be well defined but this process needs etching and lithography to create the appropriate mask. Alternatively, a different method using the Stranski-Krastanov (S-K) growth mode could form self-assembled quantum dots (SAQDs) in lattice-mismatched systems. The formation of the SAQDs is random, but the size and density of the SAQDs are predictable. The properties of the SAQDs are highly
dependent on growth conditions such as substrate temperature, deposition rate, and deposition time, and these parameters need to be well calibrated to form the desired structure. Strain is crucial in SAQDs formation, so materials need to be carefully chosen to supply the proper amount of lattice mismatch, generally >4%.

SK growth mode occurs between the growths of highly strained materials. For example, InAs (a=6.0584Å) on GaAs (a=5.6533Å) produces a 7.2% lattice mismatch. The driving force for the SK growth mode (2D-to-3D transition) is the relaxation of the elastic energy which builds up when the thickness of mismatched epilayers increases. At the beginning of the deposition process, InAs first forms a thin 2D layer called the “wetting layer (WL)”. As the deposition continues, the thickness of wetting layer passes a certain thickness call the critical thickness (1.6ML for InAs SAQDs on GaAs), strain begins to be released by the formation of 3D islands, elastic energy is relaxed. SAQDs formed in SK mode would relax elastic energy without forming dislocations at the interfaces. Fig. 3 shows the formation of SAQD in the SK growth mode.

Fig. 3: Schematic representation of the lattice distortion in the formation of 3D island
As discussed in the previous section, RHEED is a very useful tool to monitor the growth process, and the RHEED pattern is especially important and informative in the SAQDs growth. As the growth change from 2D growth to 3D growth, the occurrence of the 3D structure changes the streaky RHEED pattern into dots. By tacking the growth rate of the deposition and the time this transition shows up, the critical thickness of the wetting layer can be calculated. The RHEED patterns and the corresponding growth steps are shown in Fig. 4.3

![RHEED patterns and growth steps](image)

Fig. 4: SK SAQD growth and RHEED patterns
3. Characterization Techniques

a. X-Ray Diffraction

X-ray diffraction (XRD) is a characterization method to determine the atomic and molecular structure of a crystal, where the atoms in the crystal cause the X-ray to diffract into specific directions. XRD provides vital information on the composition and strain of III-V heteroepitaxial layers used in optoelectronic devices.

The foundation of XRD analysis is the Bragg law:

\[ n \cdot \lambda = 2d \sin \theta \]

where \( n \) is the order of the corresponding diffraction, \( \lambda \) is the X-ray wavelength, \( d \) is the lattice constant and \( \theta \) is the incident angle. The lattice mismatch could be calculated as:

\[ \frac{\Delta d}{d} = - \cot \theta \cdot \Delta \theta \]

The difference of the lattice constant between the two layers could then be obtained by measuring the separation of the diffraction angles. Fig. 5 shows a schematic illustration to measure the lattice mismatch between two layers.
Fig. 5: Diffraction from epitaxial layer and substrate

Fig. 6 shows an example of the use of the rocking curve of XRD measurement.\(^5\) The sample is grown on an InP substrate, one thin layer of AlAsSb is grown and then a thin layer of InGaAs is deposited. The lattice mismatch of the layers \(\Delta d/d\) with respect to the InP substrate could be calculated from their peak positions away from the substrate, and is \(\sim 2 \times 10^{-3}\) for AlAsSb and \(\sim 1 \times 10^{-4}\) for InGaAs. The thickness and composition could also be simulated by matching the fringes next to the main peak, and the growth rate can be calculated from the deposition time which is \(\sim 650\text{nm/h}\) for AlAsSb and \(300\text{nm/h}\) for InGaAs.

![HR Rocking Curve](image)

Fig. 6: An example of the XRD-rocking curve of a 70 nm AlAsSb and 230 nm InGaAs structure grown at 490\(^\circ\)C on InP. The bottom line shows the simulation fit.

b. Atomic Force Microscopy
Atomic force microscopy (AFM) is a very high-resolution scanning probe microscopy to characterize the surface morphology of the sample. The AFM has a cantilever with a sharp tip at its end to scan the specimen surface, the tip is very sensitive to the surface forces such as mechanical contact force, van der Waals forces etc., and the interactions between the tip and surface could give information on the surface morphology of the sample. AFM is very useful to characterize surface SAQD morphology, dot density, and height, these parameters can be determined over a large surface area. The type of AFM that is often used to characterize SAQD is the tapping mode, the tip intermittently contacts the surface and it has sufficient amplitude to prevent the tip from being trapped by adhesive forces from the surface. Fig. 7 shows an example of $1 \times 1 \, \mu m^2$ AFM image of InAs SAQDs formed on GaAs, the InAs coverage in the sample is 3.1ML. The average SAQDs height is around 9nm and the density of the SAQDs is around $4.6 \times 10^{10} \, cm^{-2}$. 
c. **Electron Microscopy**

Electron microscopy uses high voltage electron beams to enhance image resolution. Transmission electron microscopy (TEM) is always used to characterize SAQDs. The sample preparation is difficult in TEM characterization, and focused ion-beam equipped scanning electron microscope (FIB SEM) is usually used to prepare the sample. To have adequate amount of electrons to transmit through the sample, the sample needs to be prepared to be thin enough (<50 nm). The sample preparation is a combination of depositing Pt and milling the sample with the ion beam. The sample is then placed on a TEM grid for analysis. An example of SAQDs under TEM is shown in Fig. 8.7

![Cross-sectional TEM images of InAs/GaAs SAQDs with InAs thickness of (a) 2.3 ML, (b) 3.4 ML.](image)

Fig. 8: Cross-sectional TEM images of InAs/GaAs SAQDs with InAs thickness of the (a) 2.3 ML, (b) 3.4 ML.
TEM images of the cross-section of InAs/GaAs SAQDs with (a) 2.3ML, (b) 3.4ML InAs coverage are shown in Fig. 8. SAQDs were clearly observed in the sample with 2.3ML InAs coverage, no stacking faults or dislocations were observed in the sample. However, for the 3.4ML sample, the TEM image shows the occurrence of threading dislocations and stacking faults in the GaAs cap layer when the InAs coverage is increased to 3.4ML. This example shows that defects are very obvious under TEM, and we can use TEM to characterize the material quality of the SAQDs.

d. Photoluminescence

Photoluminescence (PL) is a process of spontaneous emission of photons from a material when optical excitation is applied. It is useful to measure the energy levels in semiconductor samples, and extract important information about the sample such as band gap, band alignment, and activation energy. Fig. 9 shows a diagram of a PL setup. A laser is directed onto the sample by an optical system to excite the material, chopper is often utilized at this stage and is synced with a lock-in amplifier to extract useful signals. Samples are placed in a cryostat for low temperature measurement. When the laser beam excites the sample, electron-hole pairs are created and then they recombine to emit light. The emitted light from the sample is directed into a spectrometer, a diffraction grating is used inside the spectrometer to select wavelength, and a photo-detector is attached at the opening of the spectrometer to measure the intensity of light at each wavelength.
PL measurement is extremely useful in SAQDs characterization, an example is shown in Fig. 10. Valuable information can be extracted from the PL measurement: the PL intensity is affected by the optical quality of the SAQDs, the PL peak energy is dependent on the sizes and composition of the SAQDS, and the FWHM is sensitive to the size and the shape distribution of the SAQDs. As can be seen in Fig. 10, the ground state emission and the first excited state emission can be clearly observed, and as the InAs coverage increases (suggesting SAQDs with bigger dimensions), the confined energy is lowered due to the increase of SAQD size.
Time resolved photoluminescence (TRPL) is also a useful measurement to study the optical dynamic process within the sample. A monochromator is used to select a single wavelength to be directed into a photo-detector. A pulsed laser beam acts as a trigger of the photoluminescence, the PL emission will decay over time and this decay process is recorded by the photodetector. The decay process of the PL can provide information about the carrier dynamics taking place in the sample. As shown in Fig. 11, TRPL shows the decay process of SAQDs at different emission wavelengths, and they can be well described by a single exponential decay process.\(^9\)
Fig. 11: TRPL spectra of InAs/GaAs SAQDs
4. Development of SAQDs for Intermediate Band Solar Cells (IBSCs)

a. Introduction to IBSCs

The intermediate band solar cell (IBSC) has been proposed as a next-generation, high-efficiency photovoltaic device.\textsuperscript{2} The basic concept of the IBSC is to insert an intermediate band into the original semiconductor band gap to enable sub-band gap absorption. Photon absorption from valence band to intermediate band and from intermediate band to conduction band, in addition to absorption across the full band gap, leads to an enhancement of the photocurrent. Up to 63.2\% efficiency is predicted for IBSCs, which surpasses the Shockley–Queisser efficiency limit for conventional single-junction solar cells of 40.7\%.\textsuperscript{10,11} Self-assembled quantum dots (SAQDs) have been used to create these intermediate bands, with most IBSC research focusing on well-established SAQD systems, such as InAs/GaAs\textsuperscript{11–14} and GaSb/GaAs.\textsuperscript{15} However, these material systems suffer from non-ideal band-alignment and large valence band offsets (VBO). As a result, other material systems have been proposed that better suit the requirements for high-efficiency IBSCs.\textsuperscript{16,17}

InAs SAQDs buried in AlAs\textsubscript{0.56}Sb\textsubscript{0.44} barriers lattice-matched to an InP substrate are predicted by Levy et al. to have characteristics appropriate for creating an ideal IBSC.\textsuperscript{18} The band alignments of this material system are calculated to be close to the optimal values for IBSCs using the blackbody spectrum; the transition energy from valence band to intermediate band is \(~0.7\text{eV},\) and from intermediate band to conduction band is \(~1.22\text{eV}.\textsuperscript{18,19} The InAs/AlAsSb system is expected to have type-II band alignment, which would increase the carrier lifetime in the intermediate band, lower carrier recombination
rates, and hence increase the IBSC efficiency. Also, the VBO in this material system is small,\(^{18}\) which is advantageous since large VBOs in InAs/GaAs systems is known to result in a decrease in \(V_{oc}\).\(^{16}\)

b. **Buffer Material Calibration**

Before we develop SAQDs, we need to be able to grow the buffer material – AlAsSb with decent quality. With the presence of wide miscibility gap\(^ {20}\) of the two group V materials, the growth of AlAsSb is very challenging. The arsenic to antimony incorporation ratio is extremely sensitive to variations in material fluxes, growth rate, and growth temperature. In practice, we keep the material fluxes of aluminum and antimony constant, and adjust the arsenic flux to achieve the latticed-matched composition. The composition is measured by XRD. As can be seen in Fig. 12, we can tune the arsenic composition in AlAsSb by carefully adjusting the arsenic flux, the black points are samples grown on GaSb substrate and the colored points are samples grown on InP substrate, they all show a quite consistent linear relationship between the arsenic composition and the arsenic flux.
Fig. 12: Arsenic composition in AlAsSb as a function of arsenic flux in growth

After taking a close look at the samples, we observed that samples mounted on the standard Molly block in the growth show nonuniformity across the wafer. As can be seen in Fig. 13, the sample is cleaved into 5 pieces for X-ray measurements, the composition of different regions shows significant variations. Indium bonding is then used to improve the uniformity of the growth. As can be seen in Fig. 13, the sample mounted with Indium bonding shows much less composition fluctuations across the wafer. The difference between the two mounting methods is that Molly block has more temperature fluctuation across the wafer, yet In bonding method can uniformly heat the whole sample, which helps to conduct more uniform growths.

Fig. 13: The comparison of the uniformity of the molly mounted sample and Indium mounted sample

c. Sample Description
After the development of the buffer material, we move on to study the SAQD development. It has been demonstrated that in order to grow high-quality InAs SAQDs within AlAsSb barriers, the addition of thin GaAs$_x$Sb$_{1-x}$ cladding layers adjacent to the dots is required.\textsuperscript{21} In here, this work is focused on optimizing the placement and composition of these cladding layers to enhance InAs SAQD characteristics. We investigate how the presence of Sb below and above the SAQDs affects their structural and optical properties.

Samples discussed here are grown on InP (001) on-axis (± 0.5°) substrates by solid-source molecular beam epitaxy. As$_2$ and Sb$_2$ are supplied using a valved cracker cell with cracker temperature at 900 °C. All samples have the following structure: a 500 nm AlAsSb buffer, a 5 monolayer (ML) GaAs$_{1-x}$Sb$_x$ bottom cladding layer, 7 – 8 ML of InAs SAQDs, a 5 ML GaAs$_{1-x}$Sb$_x$ capping layer, a 50 nm AlAsSb spacer, another 5 ML GaAs$_{1-x}$Sb$_x$ bottom cladding layer, and finally 7 – 8 ML InAs SAQDs on the surface [Fig. 14(a)]. We use two different compositions of GaAs$_{1-x}$Sb$_x$ for the cladding layers: $x = 0$ (i.e. GaAs) and $x = 0.05$ (hereafter referred to as GaAsSb). These compositions were chosen based both on our earlier work,\textsuperscript{21} and that of Ulloa et al.\textsuperscript{22} who improved SAQD quality in a complementary material system using GaAs$_{1-x}$Sb$_x$ cladding layer compositions in the range 0.00 < $x$ < 0.12, and the thickness of the cladding layers is thin enough so that they are fully strained to the AlAsSb barrier layer.\textsuperscript{21} Samples with four cladding layer schemes were grown [Fig. 14(b)] to investigate how various arrangements of GaAs and GaAsSb below and above the InAs affect the structural and optical properties of the SAQDs.
Fig. 14: (a) Schematic diagram of the structure investigated. 7 – 8 ML buried InAs SAQDs are separated from an identical layer of surface InAs dots by a 50nm AlAsSb spacer. The thickness of the GaAs$_x$Sb$_{1-x}$ (x=0, 0.05) cladding layers (blue) is 5 ML, (b) Schematic diagram of the four cladding schemes discussed.

The InAs SAQDs are grown via the Stransi-Krastanov (S-K) mode with the critical thickness around 4.75 ML. Atomic force microscopy (AFM) is used to study the morphology of the surface SAQDs and cross-sectional transmission electron microscopy (XTEM) is used to explore the buried SAQDs. XTEM specimens are prepared using a focused-ion beam system and imaged on a FEI Titan at 300 kV. PL measurements are performed at 77K with a 2.33 eV (532 nm) pump laser. PL emission is dispersed by a monochromator, and collected by an extended InGaAs detector with long-wavelength cut-off at 0.48 eV (2560 nm). 77K time-resolved PL (TRPL) is conducted using a 1.95 eV (635 nm) pulsed laser diode as the excitation source. We use time-correlated single photon counting to record the decay traces.

d. **AFM Characterization**
Fig. 15(a) and Fig. 15(b) show 7 ML InAs deposited on GaAs and GaAsSb cladding layers, respectively. Fig. 15(c) and Fig. 15(d) show the corresponding surfaces after 8 ML InAs deposition. In both cases, InAs deposited onto a GaAsSb cladding layer forms elongated structures, parallel to [01-1], and up to a few hundred nanometers long [Fig. 15(b), Fig. 15(d)]. In contrast, InAs deposited on a GaAs cladding layer forms quasi-circular SAQDs (Fig. 15(a) and Fig. 15(c)). The InAs SAQDs in Fig. 15(a) and Fig. 15(c) have similar areal density, $\sim 2 \times 10^{10}$ cm$^{-2}$; in Fig. 15(a) they are $\sim 4.1$ nm tall and $\sim 33$ nm in diameter, while in Fig. 15(c) they are $\sim 5.6$ nm tall, $\sim 41$ nm in diameter. Therefore, by controlling InAs coverage we can tune the average size, and hence the quantized energy levels, within our SAQDs.
Fig. 15: 1µm² AFM images showing the surface morphology of 7 ML InAs deposited on (a) GaAs and (b) GaAsSb, and 8 ML InAs deposited on (c) GaAs and (d) GaAsSb. The height scale in each is 10nm.

We now discuss the effect of Sb presence underneath the SAQDs. Sb tends to surface segregate during growth to form a Sb-rich layer, and this Sb-rich layer at the growth front promotes the known surfactant effect of Sb, delaying elastic strain relaxation via S-K growth. For samples with GaAsSb bottom cladding layers we hence see the InAs is “smeared” into quantum dashes, as shown in Fig. 15(b) and Fig. 15(d). It is however important to note that even when we use GaAs as the bottom cladding layer, Sb might still segregate from the AlAsSb to the GaAs/InAs interface due to the strong surface segregation of Sb atoms. However, the total concentration of Sb atoms will clearly be lower in this case, resulting in the circular SAQD morphology in Fig. 15(a) and Fig. 15(c). Another factor that may contribute to the elongated SAQDs in Fig. 15(b) and Fig. 15(d) is GaAsSb phase separation. Similar elongation effects have been seen in InAs quantum dashes on InGaAsP due to decomposition of the mixed-anion buffer. During growth, InGaAsP partially decomposes into columns of InAs-rich and GaP-rich regions, and this phase separation leads to surface undulations. SAQD formation tends to follow these undulations, resulting in elongation along the [01-1] direction. This decomposition effect might also exist in the GaAsSb cladding layer that leads to the elongated SAQDs shown in Fig. 15(b) and Fig. 15(d).

e. TEM Characterization
SAQDs containing defects would degrade IBSC performance since dislocation cores often act as carrier recombination centers. We used XTEM to investigate the sample with 8ML SAQDs surrounded on both sides by GaAs cladding layers since, with the most InAs coverage and the largest lattice mismatch in the cladding layer, this sample was most likely to show signs of defect formation. Nevertheless, Fig. 16(a) shows that the SAQDs are coherently strained with no sign of dislocation formation, even at high resolution [Fig. 16(b)]. One concern was that when the capping layer is changed from GaAs to GaAsSb, the presence of Sb would simply dissolve the SAQDs into a quantum well during the capping process. We hence studied the samples with 8ML InAs SAQDs surrounded by a GaAs bottom cladding layer and a GaAsSb capping layer. From the dark-field XTEM in Fig. 16(c), we still see the clear formation of buried SAQDs despite the introduction of Sb into the capping layer. Again, we see no evidence of dislocation formation in the SAQDs, even at higher resolution [Fig. 16(d)]. An interesting feature in Fig. 16(d) is the horizontal streaks in the AlAsSb layers resulting from the spontaneous ordering of the material. The bond strength of AlAs and AlSb is different, and As atoms and Sb atoms are very different in atomic size, surface segregation of Sb atoms and phase separation of AlAsSb are responsible for the Sb composition variations shown in Fig. 16(d).\textsuperscript{26}
Fig. 16: XTEM images along a \{220\} zone axis showing (a) surface and buried 8 ML InAs SAQDs surrounded on both sides by 5 ML GaAs cladding layers, (b) three buried InAs SAQDs with GaAs cap, (c) surface and buried 8 ML InAs SAQDs with cladding scheme (1) (i.e. 5 ML GaAs underneath and 5 ML GaAsSb above), (d) three buried QDs with GaAsSb cap

f. **PL Characterization**

We also investigated the influence of the different cladding layer schemes on the optical properties of the InAs SAQDs [Fig. 17(a) - 17(b)]. 77 K PL measurements of samples with 8 ML SAQDs and 7 ML SAQDs are shown in Fig. 17(a) and Fig. 17(b), respectively.

Samples with cladding schemes (1) and (3) (inset to Fig. 17(a)), both have the same capping layer (GaAsSb), but the lower cladding layer is changed from GaAs in (1) to GaAsSb in (3). Looking first at the 8 ML SAQD spectra, PL from scheme (3) (red curve) shows a red-shift of peak position and a decrease of peak intensity compared with that from scheme (1) (green curve). We see the same behavior as we compare the two schemes that have a GaAs capping layer but different lower cladding layers. PL from
scheme (4) (black curve) is red-shifted and lower in intensity than that from scheme (2) (blue curve). From these two comparisons we see that the presence of Sb beneath the InAs lowers the SAQD ground state energy and also decreases PL intensity. The red-shift of peak position with GaAsSb lower cladding layer is due to the larger effective dimensions of the elongated SAQDs shown in Fig. 15(c). These large, elongated structures are also more likely to contain more nonradiative centers, which could explain the decrease in the PL intensity.

If we instead compare cladding scheme (1) with scheme (2), (i.e. the same GaAs lower cladding layer, but GaAsSb and GaAs capping layers respectively), we see a red-shift of peak position and an increase of PL intensity from (1) (green curve) compared with (2) (blue curve). We observe the same characteristics after comparing schemes (3) and (4). Therefore, we conclude that the presence of Sb during the capping process enhances PL intensity and also red-shifts the peak position. The red-shift of peak position is caused by increased SAQD height: the presence of Sb reduces the strong SAQD decomposition that truncates SAQD height during capping with GaAs. The surfactant effect of Sb reduces In-Ga intermixing, improving SAQD compositional uniformity and increasing the PL intensity.
Fig. 17: (a) Dependence of PL emission at 77 K on different cladding schemes, for 8 ML InAs SAQDs, (b) Dependence of PL emission at 77 K on different cladding schemes, for 7 ML InAs SAQDs, (c) PL peak position at 77 K as a function of the cube root of excitation power for 7 ML and 8 ML SAQDs buried in the optimized cladding scheme (1), (d) Schematic diagram of the InAs/GaAsSb/AlAsSb band structure showing the band-bending effect discussed.

Samples with 7 ML SAQDs (Fig. 17(b)) present identical behavior to the 8 ML SAQD samples as a function of the four cladding schemes. This consistency between 7 ML and 8 ML SAQD samples confirms that we can readily control the optical properties of SAQDs by changing the cladding schemes. Each 7 ML SAQD sample spectrum shows a blue-shift in peak position compared to its corresponding 8 ML SAQD sample, since the smaller 7 ML SAQDs (Fig. 15) will have higher quantized ground state transition energies.
So, the optimal cladding layer scheme has GaAs underneath the SAQDs with GaAsSb as a capping layer. For 7 ML and 8 ML SAQDs samples with this optimized cladding scheme the peak PL energy ($E_{\text{peak}}$) was plotted as a function of excitation intensity ($I_{\text{exc}}$) [Fig. 17(c)]. In both cases the ground state transition energy increases linearly with the cube root of the excitation intensity. The observed $E_{\text{peak}} \propto I_{\text{exc}}^{1/3}$ relationship is a signature of type-II band alignment,\textsuperscript{27–29} which suggests the band structure perturbation induced by the cladding layers is insufficient to create hole confinement in the SAQDs [Fig. 17(d)]. PL emission is mainly due to recombination between electrons in the SAQDs and holes in the AlAsSb layers.\textsuperscript{21}

**g. TRPL Characterization**

Time-resolved PL gives further evidence for the type-II nature of the band structure. Fig. 18 shows the 77 K TRPL of the sample with 8 ML SAQDs buried in the optimized cladding scheme (1). Instead of the monoexponential decay process usually seen for type-I SAQDs, the decay traces for this sample are biexponential, made up of a fast and a slow process. We fit the curves using the biexponential function: $I(t) = A_1\exp[-(t - t_0)/\tau_1] + A_2\exp[-(t - t_0)/\tau_2]$, where $A_{1,2}$ are the magnitude of the two decay processes, $t_0$ is the initial time and $\tau_{1,2}$ are the time constants of the processes. At the peak emission wavelength (1600 nm), the deduced time constants are $\tau_1 = 2.19$ ns and $\tau_2 = 7.92$ ns, which are larger than the typical carrier lifetime $\sim$1 ns for type-I quantum dots.\textsuperscript{30} As we probe the time constants at different wavelengths on the PL spectrum, a strong variation in the decay time as a function of wavelength is observed, for the shortest wavelength shown in Fig. 18 (1510 nm), the time constants are $\tau_1 = 0.85$ ns and $\tau_2 = 3.42$ ns.
Similar non-monoexponential decays have been reported in GaSb/GaAs type-II SAQDs.\textsuperscript{31,32} After optical pumping, electrons are captured by the dots, locally bending the conduction band edge [Fig. 18(d)], while the holes are localized in the AlAsSb layers due to Coulomb attraction to the electrons. The rearrangement of the carrier density induced by the band bending changes the optical transition probability. The electron wavefunctions penetrate further into the barrier layer and the overlap between the electron and hole wavefunctions increases, thus leading to the initial, faster decay process $\tau_1$.\textsuperscript{33} As nonequilibrium carriers continuously recombine during the radiative recombination process, the band bending effect decreases. This reduces the wavefunction overlap and hence lowers recombination rate, leading to the slower decay process $\tau_2$.

As we increase the detection energy, the two decay processes become faster [Fig. 18]. Higher energy PL emission comes from smaller SAQDs in the dot ensemble. With deceasing SAQD size, the electron wavefunction penetrates deeper into the barrier and increases the optical matrix element, faster decay processes are thus observed.\textsuperscript{32} The low carrier recombination rates measured in this material system show the promise for enhanced IBSC device efficiency.
Fig. 18: Time dependent PL decay traces for 8 ML InAs SAQDs in the optimized cladding scheme (1) at different detection wavelengths. The dashed line is the fitting curve for the decay trace at peak wavelength.
5. Conclusions

In here, a review of MBE deposition technology is presented and several powerful characterization techniques such as XRD, AFM, TEM, PL are also presented. SAQDs are discussed to be applied in IBSCs application due to the formation of intermediate band which helps to absorb sub-band gap photons. InAs/AlAsSb material system is suitable for IBSCs application because of its ideal band alignment, and we have investigated the effects of different cladding schemes on the optical and structural properties of the type-II InAs SAQDs in AlAsSb barriers. InAs SAQDs grown on a 5ML GaAs cladding layer form discrete, lens-shaped SAQDs, while InAs deposited on a 5 ML GaAs$_{0.95}$Sb$_{0.05}$ cladding layer tends to form elongated dashes. The presence of Sb during the capping process prevents the truncation of SAQDs that occurs during capping with pure GaAs and we obtain an increase in PL intensity. We have hence shown that the optimized cladding scheme for this SAQD system has GaAs under the SAQDs and GaAsSb as the capping layer. Both PL and TRPL confirm that the band alignment is type-II. The longer carrier lifetime in this type-II band structure compared with type-I SAQDs should be beneficial for future IBSC performance.
References


