1 ML Wetting Layer upon Ga(As)Sb Quantum Dot (QD) Formation on GaAs Substrate Monitored with Reflectance Anisotropy Spectroscopy (RAS)

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III/V semiconductor quantum dots (QD) are in the focus of optoelectronics research for about 25 years now. Most of the work has been done on InAs QD on GaAs substrate. But, e.g., Ga(As)Sb (antimonide) QD on GaAs substrate/buffer have also gained attention for the last 12 years. There is a scientific dispute on whether there is a wetting layer before antimonide QD formation, as commonly expected for Stransky-Krastanov growth, or not. Usually ex situ photoluminescence (PL) and atomic force microscope (AFM) measurements are performed to resolve similar issues. In this contribution, we show that reflectance anisotropy/difference spectroscopy (RAS/RDS) can be used for the same purpose as an in situ, real-time monitoring technique. It can be employed not only to identify QD growth via a distinct RAS spectrum, but also to get information on the existence of a wetting layer and its thickness. The data suggest that for antimonide QD growth the wetting layer has a thickness of 1 ML (one monolayer) only.

1. Introduction

III/V semiconductor quantum dots (QD) are investigated for about 25 years now, mostly since they can be considered “artificial or designer atoms” [1, 2], or since they can be used to make semiconductor lasers more efficient [3], at least in principle, or since they might be employable as fundamental digital data storage units (see, e.g., [4]).

Usually QD are grown in a specific epitaxial mode, which is called Stransky-Krastanov (SK) growth [5]. This mode is based on QD self-organization during growth on a substrate/buffer with equal lattice structure (in the case of cubic III/V semiconductors α-zinc blende ( sphalerite)), but with a native layer lattice constant larger by a few percent than the lattice constant of the substrate/buffer material.

After (at most) a few monolayers of grown material serving as a wetting layer, the mechanical stress forces the deposited material into three-dimensional (3D) growth, i.e., growth into the third dimension. Nano-islands typically with flat, pyramidal shape form statistically at the growth front [1, 2]. If the material supply is cut off soon enough (after a few seconds), the islands will stay so small, that they can be considered 3D quantum wells, i.e., QD, presupposed that the surrounding materials have larger band gaps, acting as potential barriers for carriers.

SK growth had been shown for InAs QD on GaAs substrate and innumerable contributions have been made by other authors in this context (see, e.g., again [1, 2]).

There is less experience in the community with Ga(As)Sb (so-called antimonide) QD on GaAs substrate, but even in this regard quite a number of papers have been published...
(e.g., [4, 6–20]). Very interesting results have been achieved by the Huffaker group [12–15], which brought the aerial density of antimonide QD to 290 μm⁻². The authors of the current contribution have been successful in increasing the aerial QD density even further, i.e., to values of about 1000 μm⁻², which lets the QD nearly abut in the growth plane [16–20]. E.g., dense lying QD are important to improve semiconductor laser efficiency.

There is a disagreement in the community on the existence of a wetting layer and its thickness for antimonide QD growth. Sometimes photoluminescence (PL) peaks (measured ex situ after the epitaxial process) are attributed to wetting layers, although the spectral peak positions (after all a thin wetting layer before QD growth should optoelectronically have the properties of a very thin quantum well) and peak heights (thin wetting layers should have very small to vanishing PL peaks due to their vanishing luminescent mass) do not fully support the assumption of a thin wetting layer. This contribution wants to help to settle the case.

First we show results of ex situ PL measurements as well as atomic force microscopy (AFM). Then we verify that reflectance anisotropy/difference spectroscopy (RAS/RDS) is also capable of identifying the formation of a wetting layer as well as of the antimonide QD themselves—in situ and real-time.

Indeed other groups and these authors have already shown that RAS can be used to monitor SK growth of InAs QD on GaAs [21–24] and of antimonide QD on GaAs [20, 25–30], since the QD RAS spectra considerably differ from those of layers of similar composition. Here—for antimonide QD growth—we report on further details of the signal peaks in RAS spectra: they suggest a wetting layer of just one monolayer (1 ML) (for cubic III/V semiconductors, a monolayer constitutes a double atomic layer, one atomic layer made of atoms from the group III element the other made from atoms of the group V element; sometimes 1 ML is also taken as a unit for thicknesses; in that case 1 ML equals half a lattice constant and double the thickness of an atomic layer).

2. Some Growth Details

Ga(As)Sb QD formation on GaAs substrate/buffer is initiated by supply of Ga and Sb atoms only. Due to As and Sb diffusion and intermixing [31] and without further action the resulting QD are not made of pure GaSb, but rather of Ga₆Sb₆ with a relatively high As content of up to x = 72% in our case. In order to avoid a high As content x in the QD, they are stabilized in an Sb atmosphere (background pressure) for 10 s, before we grow a 50 nm thick GaAs cap.

Photoluminescence (PL) measurements were performed and atomic force microscope (AFM) images were taken as well—for six samples with different nominal coverage of 1-6 ML. Since the QD would immediately oxidize/degrade upon the air-break during the transport of the samples from the MBE machine to the AFM, a special sample design had to be used, which is given in the top of Figure 1. Actually two identical QD “films” were grown with a 50 nm thick GaAs layer in-between, which has been called “cap” above (this layer is thick enough to compensate for the stress of the QD; a smooth, nonstrained surface can be assumed after growth of the “cap”). The bottom QD layer was taken for retrieval of the PL spectrum (and before of the RAS spectrum), and the top QD layer was used for the AFM measurements.

3. Experimental PL and AFM Results

The AFM micrographs in Figure 1 reveal that no QD have been grown for the case of 1 ML nominal coverage, but for all other used coverages (2-6 ML). This finding supports the conclusion that a 1 ML thick wetting layer exists.

In Figure 2, the corresponding PL spectra are given. In case of no growth or growth with a coverage of 1 ML only (black curve in the main graph and identically in the inset) there is no peak to be attributed to quantum dots (QD).

The (always) observable double peak is related to the GaAs substrate/buffer. The double peak is caused by excitonic levels and appears, whenever the GaAs buffer is extremely pure [32].

For coverages of 2-6 ML, there is one additional peak each. It is attributed to the occurrence of Ga(As)/Sb QD. The peak for 6 ML nominal coverage is small and broad, but noticeable.

Since only the double peak of the buffer can be observed for 1 ML coverage, again it can be concluded that no QD arose in this case and that indeed a wetting layer exists upon Ga(As)/Sb QD growth, but that it has a maximum thickness of 1 ML.

4. RAS Principle and Signal Representations

RAS/RDS had indeed been developed for in situ epitaxial growth control by Aspnes, Harbison et al. [33–46] and has mostly been employed for MOCVD (metal-organic chemical vapor deposition), but also for MBE (molecular beam epitaxy), as in our case. RAS signal peaks in the spectra are often, but not always related to orderly oriented electronic surface states (electric dipoles at the crystalline surface) [47–53].

In Figure 3, a typical RAS beam path is sketched. A broadband light source, typically a Xe lamp (with photon energies between 1.5 and 4.5 eV), is used. The emitted originally nonpolarized light wave is linearly polarized with the help of a polarizer. Then the wave enters the epitaxy vacuum chamber via a viewport and impinges (nearly) perpendicularly onto the growth front on the sample surface.

The light wave can be considered as composed of two wave parts with orthogonal linear polarization. Whenever the plane of polarization of one wave part incorporates a main crystal axis, in case of cubic crystals the plane of polarization of the other wave part will include another main crystal axis.

For the hypothetical case of a perfectly flat and homogeneous surface normal incidence should not give any differences in reflectance for the two wave parts (not even a plane of incidence can be defined in the case of normal light incidence). But surface anisotropies like, e.g., the above-mentioned orderly arranged electric dipoles (especially prevalent for crystalline III/V semiconductors due to their ionic bond portion) break the symmetry and a
Figure 1: Sketch of layer sequence and atomic force microscope (AFM) images of GaAs surfaces after GaSb growth with nominal coverages of 1-6 ML. The lateral scaling is equal in all cases, and the vertical/gray scaling is not. For a coverage of 1 ML no QD can be observed. For a nominal coverage of 6 ML the QD are too close to each other to be reckoned as completely separated. E.g., for the pyramidal QD and 3 ML nominal coverage the side length is 27 nm and the height amounts to 4 nm.

Figure 2: Photoluminescence (PL) spectra for the cases of GaSb growth with nominal coverages of 1-6 ML. The (single) peaks can be attributed to the occurrence of Ga(As)Sb QD, the always occurring double peak to excitonic levels of the pure GaAs buffer [32]. For 1 ML no QD peak is observed. The black curve in the inset is identical to the black curve in the main graph.
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2 main crystal axes
wafer with flat viewport of epitaxy chamber

slightly elliptical light polarization
photoelastic modulator
(dynamic λ/2 wave-plate)

(nearly) surface-normal incidence
polarizer
from Xe lamp

to monochromator

Figure 3: Perspective sketch of a RAS beam path. On the contrary to the drawing, the real angle of light incidence onto the wafer surface is ≈0.

The reflectance difference will occur for the two wave parts. The genuine RAS signal is

$$\frac{\Delta R}{R} = \frac{R_{[-110]} - R_{[110]}}{\langle R \rangle}$$  \hspace{1cm} (1)

with the symbol \( R \) for reflectivities/reflectances and taking the main crystal axes \([-110]\) and \([110]\) exemplarily here. \( \langle R \rangle \) is the mean reflectivity, averaged over the two wave parts. Typical signal levels are around \(10^{-3}\), but the technique is sensitive down to around \(10^{-5}\).

In general, due to the reflectance difference the state of polarization of the overall wave should change from linear to slightly elliptical upon reflection at the growth front (see Figure 3). In order to detect the ellipticity of the wave's state of polarization, the reflected light wave is monitored with the help of a photoelastic modulator (PEM) (with 50 kHz modulation frequency), used as a switchable \(\lambda/2\) wave-plate, a second polarizer (analyser), and finally a monochromator with a detector. The PEM in connection with the analyzer allows for periodical detection of both linearly, orthogonally polarized wave parts. (During epitaxy the wafer is usually rotated with \(1/s\), so that there are only certain angular windows of the sample orientation (occurring periodically and twice per cycle), when/where the reflectances can be measured. The software of the RAS system manufacturer is tuned such that only absolute values of the RAS signal acc. to (1) are extracted.)

Due to the normal light incidence typical ellipsometric information is deliberately suppressed. The retrieved information is rather directly related to the ordered and oriented anisotropies at the surface (and possibly to optical Fabry-Perot resonances from the currently grown layer with increasing thickness).

Figure 4 contains a photograph of our R450 MBE system (by DCA Oy, Turku, Finland) with the EpiRAS apparatus (by Laytec, Berlin, Germany) in front of the central flange which is oriented normal to the wafer/sample surface.

There are different ways to represent the RAS signal data. For a \textit{RAS color plot} the signal level is color-coded and given simultaneously in dependence on photon energy and on elapsed epitaxy time (a colored two-dimensional plot). For a \textit{RAS transient} the signal height at a specific photon energy is plotted over elapsed time. A \textit{RAS spectrum} contains the RAS signal for a fixed point in time in dependence on photon energy.

5. Experimental RAS Results

Figure 5 contains RAS spectra (for 11 photon energies with 0.3 eV separation between adjacent spectral sampling points) for different objects [54, 55], i.e.:

1. a fresh GaAs surface during epitaxial growth on a GaAs substrate/buffer without As stabilization (solid red line),
2. a fresh GaSb surface during epitaxial growth on a GaSb substrate/buffer without Sb stabilization (solid green line),
3. surfaces with \textit{definite} Ga(As)Sb QD on GaAs substrate/buffer—the solid black line has been retrieved as an average over more than ten quantum dot growths and RAS measurements accompanied by the verification of QD existence with PL and AFM,
4. after nominal coverage of the substrate/buffer (the nominal coverage is the amount of material, which is supplied for QD growth; it is measured in monolayers (ML), although QD instead of just monolayers are grown) with 1 ML, 2 ML, or 3 ML of GaSb (broken dark-blue, broken purple, broken light-blue line, respectively).
Figure 4: Photograph of the R450 MBE machine by DCA Oy, Turku, Finland, with the RAS system EpiRAS by Laytec, Berlin, Germany in front.

The RAS spectra in Figure 5 exhibit clear distinctions for the cases GaAs layer, GaSb layer, and definite Ga(As)Sb QD (solid lines). This is an important result and it will be a necessary condition, if Ga(As)Sb QD growth is intended to be identified with RAS. E.g., there is a distinct minimum at ≈2.4 eV photon energy and a maximum at around 1.8 eV for the definite QD, while it is the other way around for the GaSb layer (on GaSb substrate/buffer). The double standard deviation $2\sigma = 2 \cdot 0.034$ (i.e., the error bar) of the signal data points is smaller than the height of the characteristic spectral RAS peaks; thus the peaks are considered significant.

Moreover, for the growth of just 1 ML, the RAS spectrum is completely different to the spectra of the GaSb layer and for higher nominal coverages, whereas the cases with 2 ML or 3 ML show similar spectra to the case with definite QD formation. This result alone already indicates that a wetting layer exists and that it has a maximum thickness of 1 ML.

That means that the occurrence of the wetting layer and/or of QD can already be identified undoubtedly in situ and real-time upon SK antimonide QD growth, if RAS is employed. Any tedious ex situ verification is not necessary.

6. Conclusions

Reflectance anisotropy/difference spectroscopy (RAS/RDS) has been used to get in situ and real-time evidence of the existence of a wetting layer in Ga(As)Sb (antimonide) quantum dot (QD) formation on GaAs substrate in the Stransky-Krastanov (SK) growth mode and of its thickness.

The solid-state physics result is that Ga(As)Sb QD formation on GaAs substrate/buffer incorporates the initial formation of a wetting layer with a thickness of just one monolayer (1 ML).

The technological result is that the RAS spectra for epitaxial growth with different nominal coverages of a couple of monolayers yield the same results in situ, as photoluminescence (PL) spectra and as atomic force microscope (AFM) images deliver ex situ. This finding includes the opportunity to make QD growth processes easier to be controlled.

A corresponding conclusion should very likely be drawable for QD growth of any suitable III/V semiconductor combination due to the ionic bond share and related surface states of III/V semiconductors.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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