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The Metalorganic Vapour Phase Epitaxy Growth of A^{III}B^V Heterostructures

Observed by Reflection Anisotropy Spectroscopy

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Reflectance anisotropy spectroscopy is a useful technique used for *in situ* observation of the metalorganic vapour phase epitaxy growth, because it does not require vacuum in the reaction chamber. With this method we are able to observe the quantum dot growth, the incorporation of indium or antimony atoms in the layer or the monolayer growth of GaAs. We can also estimate the amount of InAs needed for the quantum dot formation, the time necessary for the quantum dot growth or reveal the unintended growth of InAs quantum dots from large dissolved InAs objects.

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1. Introduction

The study of the quantum dot (QD) growth is very important for the proper understanding of the processes that lead to their formation. Reflection anisotropy spectroscopy (RAS) [1, 2] is one of a few techniques to observe in situ the growth of epitaxial layers and quantum dots prepared by metalorganic vapour phase epitaxy (MOVPE), which is unique, other techniques are usually ex situ [3]. This method is used across different scientific fields like physics [4] or biology [5]. Its biggest advantage is that it does not need vacuum for the measurement, as it is usual for other measuring techniques such as different kinds of electron diffraction. This advantage comes with the optics behind the measurement, when a difference between two reflectances obtained from two perpendicular directions is measured. This is also the reason why this optical method is able to measure surface properties, while the bulk ones are subtracted.

2. Experimental

RAS method is based on the measurement of the difference between the reflectances in two crystallographic directions [-110] and [110]. From the RAS signal and its oscillations it is possible to estimate the growth rate, thickness of an InAs layer initial for the QD growth (accuracy less than 1 monolayer (ML)) or the presence of particular atoms on the surface (indium or antimony) during the growth of InAs QDs covered by GaAsSb strain reducing layer (SRL). The basic principle may be described by the equation

$$\frac{\Delta r}{r} = 2 \frac{r_{[-110]} - r_{[110]}}{r_{[-110]} + r_{[110]}},\tag{1}$$

where r with proper index means the reflectance in particular crystallographic direction. The experimental scheme is shown in Fig. 1.



Fig. 1. Experimental setup scheme of the RAS measurement [6].

After going through the path, the light is detected and the intensity is measured. By this method only the surface is observed, the signal from the isotropic bulk is subtracted in final. There are two different modes of measurement: time resolved for observation of the kinetic of the process (QD formation, GaAs monolayer oscillation) on one specified wavelength with high time resolution or spectroscopic mode for complex observation of the growth in wide range of energies but with low time resolution of 30–60 s. The spectroscopic data can be displayed in a form of colorplot which shows a complete RAS signal record for wide range of energies during the growth.

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RAS measurements were performed on LayTec Epiras 200 TT equipment fixed to Aixtron 200 MOVPE machine. All growth processes were performed in a pure H_2 atmosphere in a quartz horizontal reactor at low pressure of 70 hPa from common organometallic sources [4].

3. Results and discussion

RAS enables the observation of many different mechanisms that take place on the surface; here few of them related to the preparation of InAs/GaAs QDs covered by GaAsSb SRL will be described.

3.1. GaAs monolayer growth oscillations observation

During the island growth of GaAs, a signal oscillates at the energy of 2.65 eV for one ML. This is caused by the two different surface reconstructions that switch during the growth of one ML. When GaAs islands are formed, the arsenic atoms are desorbed from the island edges and the surface reconstruction becomes $\beta 2(2 \times 4)$. When a complete ML is formed, the arsenic atoms are incorporated and the reconstruction becomes $c(4 \times 4)$. Because those two reconstructions have a large difference in the signal value, the total signal oscillates between higher intensity (island, large amount of edges and less arsenic) and lower intensity (levelled layer, no edges, more arsenic) at 2.65 eV. Our results on GaAs growth are shown in Fig. 2. From this graph, the growth speed may be estimated as well as the time, when the metalorganic reaches the reactor chamber (here it takes TMGa 1 s to reach the reactor chamber).



Fig. 2. Monolayer oscillations of the GaAs growth.

3.2. Optimal amount of InAs for a QD formation

For this measurement, time resolved mode with the resolution of 1 s at 4.2 eV was chosen for the observation of a QD formation. From the RAS spectrum, the thickness of the initial InAs layer can be estimated. The signal maximum is obtained for one ML of InAs, and since the deposition time is known, it is possible to estimate the total amount of InAs, see Fig. 3.



Fig. 3. RAS spectrum for estimation of the proper amount of InAs for a QD formation; QDs are formed for 1.8 ML thick InAs layer (red line), 1.5 ML InAs (blue line) is insufficient.



Fig. 4. PL spectra of samples with 1.8 ML and 1.5 ML of InAs for a QD formation, only sample with 1.8 ML has QDs and evince PL.

The blue line in Fig. 3 corresponds to a sample with 1.5 ML and the red line to a sample with 1.8 ML. The QD growth is revealed by the increase and then a decrease of the RAS signal during the waiting time (WT); this is observable only for the red line, where the amount of InAs is sufficient for the QD formation. This conclusion is supported by the photoluminescence (PL) measurements, see Fig. 4. For the red line the QDs evince PL around 1300 nm, while the blue line sample presents no QD signal since QDs were not formed.

3.3. Waiting time optimization

Optimal amount of InAs for the QD formation is 1.8– 2.1 ML. The time needed for the QD self-assembly is characterised as WT and has an impact on the QD size. Again, the time resolved mode was used at 4.2 eV and the RAS spectrum is shown in Fig. 5; the blue line sample with WT of 14 s and the red line sample with WT of 30 s. During the 14 s, QDs were formed and evince PL. On the contrary, for the sample with 30 s WT (the red line) the time was overly long and large InAs objects (due to the Ostwald ripening) with no PL signal were formed and only a few QDs were created; for the results on the PL measurements, see Fig. 6.



Fig. 5. RAS spectra of samples with different WT; for 14 s WT (blue line) QD were formed, for 30 s WT (red line) the time was overly long and QD coalesced into large objects, this process is called Ostwald ripening.



Fig. 6. QDs were formed and evince PL for a sample with 14 s WT (blue line), for the WT of 30 s (red line) QDs coalesced into large objects that do not have a PL.

3.4. Indium and antimony atoms incorporation

Complete growth of InAs/GaAs QDs covered by GaAsSb was recorded in the colorplot mode, see Fig. 7. Single slices from the colorplot are the spectroscopic mode spectra, see Fig. 8. From those it is possible to understand the growth process.

In Fig. 8a, an intense signal at 2.5 eV is obtained from the indium atoms present on the growth surface. This is the time, when InAs layer is deposited. Then, in Fig. 8b,



Fig. 7. Complete RAS spectrum of a growth of InAs QDs covered by GaAsSb SRL.



Fig. 8. RAS spectra in spectroscopic mode for the growth of InAs QDs covered by GaAsSb SRL.



Fig. 9. HRTEM image of an InAs QD covered by a GaAsSb SRL on which an InAs QD was subsequently overgrown originating from large InAs dissolved objects.

InAs QDs are being covered by GaAsSb SRL, In atoms are still present on the surface, but the signal decreases because they are being covered; the presence of Sb atoms is seen from the RAS intensity drop at 3 eV. In Fig. 8c, the re-growth of GaAsSb SRL by GaAsSb starts, the drop at 3 eV disappears, but the signal from In atoms at 2.5 eV is still present. This means that the In atoms are still present on the surface. Those In atoms come from large InAs objects that were dissolved during the growth of GaAsSb SRL, but at the same time, those atoms were not incorporated into the layers because they float on the surface. Once the GaAsSb layer is deposited and GaAs layer starts to cap the structure. In atoms are incorporated and the signal at 2.5 eV disappears, see Fig. 8d. These atoms then form unintended InAs QDs over the first ones, which was proved by high resolution transmission electron microscopy (HRTEM) observations shown in the corresponding image of Fig. 9.

4. Conclusions

By the RAS measurement we were able to observe in situ the growth of InAs/GaAs QDs covered by GaAsSb SRL prepared by MOVPE. We could estimate the proper amount of InAs and the length of WT needed for a QD formation. We could also determine the growth speed. This method also helped us to reveal unintended growth of QDs. In atoms for those QDs arise from the dissolution of large InAs objects and are incorporated after the growth of GaAsSb SRL. This was evidenced by HRTEM observations. Based on all results, RAS method can be recognized as an indispensable characterization method for *in situ* observation of the MOVPE growth semiconductors with cubic lattice.

Acknowledgments

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