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On the shape formation of the droplet epitaxial quantum dots

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ABSTRACT

In this paper, the shape evolution kinetics of droplet epitaxially grown QDs is investigated. Here, the growth parameter dependent of two distinct QD shape regimes is discussed. We show that the QD shape is determined by the size and the contact angle of the initial droplet. Furthermore, the surface tension dependence on the droplet size is also discussed. Finally, the temporal course of the crystallization process is investigated.

1. Introduction

The growth of self-assembled quantum structures has been nowadays intensively investigated as they can have both fundamental physical and also practical applications. It is very important to understand their growth kinetics and the knowledge about their shapes is especially significant. The archetype of these nano-structures is the lattice-mismatched InAs/GaAs system [1,2]. The preparation of self-assembled quantum dots (QDs) by applying droplet epitaxy is an encouraging alternative to the strain-induced InAs QD formation, since compared to strain-induced technique the QD formation is more flexible regarding the choice of the QD material. It is already verified that fabrication of strain-free GaAs QDs on AlGaAs surface is possible [3,4]. The production of InGaAs QDs with controlled In content has already been carried out, too [5,6]. Not only the material variety, but the shape can also be various such as QD, quantum-ring, double-ring, and nano-hole [7–10].

The electronic structure of a QD, which determines the electrical and optical properties, is strongly influenced by its shape [11,12]. The shape of these quantum structures depends strongly on the growth parameters; therefore, it is very important to understand their growth kinetics. As we demonstrated earlier, the shape of the QDs depends on their volume and also on their density [13]. Our earlier investigation shows that the nanostructure dependence on the temperature can be divided into two distinct regions. Under 200 °C, the temperature dependence follows a so-called scaling law behaviour. While over 200 °C region is the onset of the coarsening by Ostwald ripening [14]. In this paper, we focus on the morphological and temporal formations of the differently shaped QDs, formed from the initial Ga droplets based on the surface tension. Here, two types of QD are investigated. One of them, the larger QDs are strongly truncated pyramid-like, with side-facet angles about 55°, while the other one, the smaller QDs are slightly truncated pyramid-like with side-facets 25° [13].

2. Experimental preliminaries

The growth experiments were performed in a solid source molecular beam epitaxy system equipped with a valved arsenic cracker cell. The evolution of growth front was monitored with reflection high-energy electron diffraction (RHEED) method. On $Al_{0.3}Ga_{0.7}As$ (001) surface, droplet epitaxial GaAs QDs were formed. The main steps of the droplet epitaxial process were as follows. After the preparation of $Al_{0.3}Ga_{0.7}As$ surface, the samples were cooled down to 200 and 250 °C, and Ga was deposited with the flux of 0.19 and 0.025 ML/s without the arsenic flux, respectively. The total surface coverage was $\Theta = 3.75$ ML. After a few seconds of waiting time following the Ga deposition, annealing was performed at 350 °C temperature under 5×10^{-5} Torr arsenic pressure. The continuous RHEED monitoring was carried out along the [1–10] direction. After the growth (and one case, before crystallization), the QDs were investigated with atomic force microscopy (AFM) in tapping mode, where the tip apex has below 10 nm of radius [15]. In one case, the initial droplet was also investigated. The reason is discussed later. More detailed experimental description is published previously elsewhere [13].

3. Results and discussion

3.1. Droplet formation

As the first step in QD production, Ga droplets are formed on the substrate surface. As the second step, the droplets are transformed into QDs during the crystallization process. The investigation of droplet formation is the basic step towards the understanding of QD development, thus in one case the preparation procedure of the QDs was interrupted before crystallization. This particular sample was quenched and inspected by AFM immediately after the Ga droplets were formed.

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On another set of samples, the Ga droplets were formed under identical technological parameters but the step of crystallization was also carried out, in order to compare the two kinds of samples. The density and the size of QDs were identical to that of the Ga droplets. In the upper part of Fig. 1, the geometrical setting of the electron beam of the RHEED gun during the structure evolution can be seen. The RHEED picture characterizes mainly the nano-structures on the surface, because the open surface is in "shadow" for the electron beam (see the label of the figure). In the lower part of Fig. 1, the tracking of the surface evolution by the RHEED method is given; the first picture with sharp RHEED streaks is characteristic on the surface before the Ga deposition (Fig. 1A). The streaky RHEED picture becomes diffused because of the electron beam crossing the liquid aggregate (droplet) (Fig. 1B). The next pictures show the RHEED screen during the QD formation under the arsenic atmosphere; immediately after the shutter opening (Fig. 1C) and a few minutes later (Fig. 1D).

The original shape of the droplets formed on the surface is conserved during this investigation due to the residual adsorbate on the droplet surface. This adsorbate effect was observed also at ultra-high vacuum condition, under 10^{-10} Torr [16–18]. The geometry of these clusters follows the law of the surface and interface energy minimization [19–25]. Over 200 °C, the size and the density of the initial droplet are determined by the process of Ostwald ripening [14]. The Ostwald ripening means the growth of larger clusters at the cost of smaller ones [26–32]. Furthermore, the shape of the droplets is determined by the surface tension in the liquid aggregate and by the wetting properties at the interface. The contact angle (the angle of the tangent at a liquid/vapour interface meets the solid surface, called three-phase line) is determined by the balances of surface and interface energies.

In practice, droplets (with mm size) are used for surface such characterization [33–35]. Surface tension is caused by the intermolecular forces on the surface of the liquid [36]. This tension is an effect within the surface layer of a liquid that can be modelled as that layer behaving like an elastic sheet [37]. For our calculations, we would like to know the thickness of the surface sheet. In the case of a large droplet radius, the thermo-dynamical description of the tension is widely used [38–42]. If

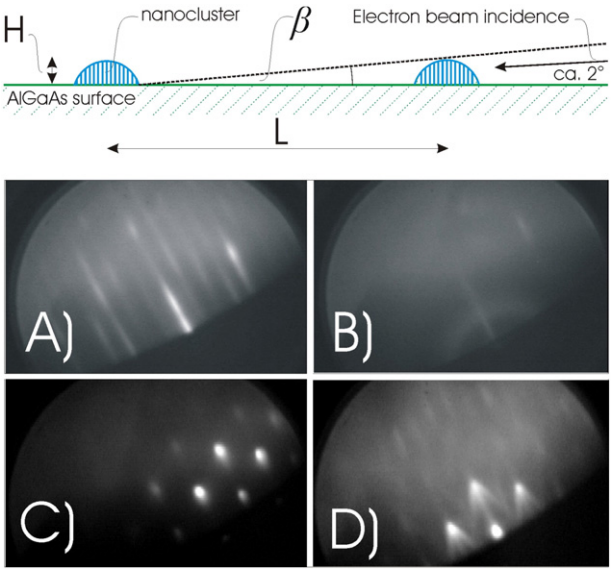

Fig. 1. Upper part: The RHEED geometry on the surface. When $N_1 = 1.2 \times 10^{10}$ cm^{-2} and $N_2 = 4.4 \times 10^8$ cm^{-2}, the average height (H) of the droplet and the characteristic average distance (L) between these nanostructures are $H_1 = 7$ nm, $H_2 = 32$ nm and $L_1 = 90$ nm, $L_2 = 477$ nm, respectively. The RHEED picture is characteristic to the nano-structures, because $\beta_1 = 4°$ and $\beta_2 = 3.8°$ are larger than the incidence angle (about 2°) of the electron beam. Lower part: RHEED pattern during the dot formation. A) Streaky diffraction picture of flat AlGaAs surface [1–10]-azimuth; B) RHEED picture becomes diffuse during formation of Ga droplet; C) spotty picture of electron intensity develops after opening of arsenic cell; D) chevron tails are formed during the crystallization of aggregate.

the droplet radius decreases, this description becomes less and less useful [43–45]. The relation between the mean inner potential and the surface tension is known [46,47,56]. In the nano-range, the mean inner potential drastically changes [46]. This phenomenon can give support to estimate the "surface sheet".

In the word of nano-sized clusters, there is a lot of unknown and surprising properties yet. The size dependence of the melting point already also counted as evidence [48]. The further reduction of the size causes the increasing of the melting point [49]. A similar interesting question is the thickness and the properties of the surface sheet, which are an influence to the shape of the nano-clusters. The extension of the thermodynamical description – used in a macroscopic case – to the nano-sizes is well useful in certain cases [40–42]. According to another approach, the bond distances need to be considered. There is a mechanical stress, where the bond distances are different from the bond distances of the bulk material. The diffraction investigations show that in the nanocluster the lattice constant around a few times 10 nm is similar to the bulk material, but under 10 nm is different from that [50,51]. We will calculate with sheet thickness, with this changed lattice constant as a "surface" sheet thickness, which corresponds well to the previous experiments and values, estimated on a theoretical basis [36,37]. In this way, we can distinguish two types of clusters or droplets. One of them has a larger radius than the sheet thickness (case i) and another one has a radius below this value (case ii). Of course, the change of the lattice parameter between the surface edge and bulk material is not abrupt but continuous, so here the defined surface sheet thickness is an approach only.

Inside this very thin sheet, the intermolecular forces are independent of the length of the sheet. Therefore, the behaviour of these intermolecular forces differs fundamentally from the force in an elastic membrane. On a macroscopic scale, the interaction between these forces at the three interfaces is independent of the dimension of the droplet [34,35]. In this case the forces in the surface sheet are independent of the area and depend only linearly on the thickness, therefore on the number of interacting molecules in the unit area. This description is valid if the dimensions of the droplet are much larger than the thickness of the surface sheet. If the dimension of the droplet decreases to the nano-range, and the size becomes comparable with the dimension of the thickness of surface sheet (approx. 10 nm), the shape of the droplet (and also the contact angle) changes.

The surface tension depends on the temperature. It decreases with increasing temperature (Eötvös law) [37], and also decreases with increasing ambient pressure [52]. The surface wettability (and also the contact angle) depends very strongly on the properties of the substrate surface. In order to characterize the GaAs/Ga surface tension, molten Ga droplets were investigated on pure GaAs substrate in hydrogen atmosphere at various temperatures [53]. At 852 °C, which is typical to the liquid phase epitaxy, the contact angle is 28°. The temperature coefficient is 3.6°/100 °C [53]. According to these data, at 250 and 200 °C the contact angles should be around 50° and somewhat larger, respectively. In our case, the droplets are in vacuum, thus the pressure conditions are different, therefore the contact angle differs somewhat from that of the calculated values. Furthermore, it was found that in the AlGaAs substrate, the contact angle increases with the increased Al content [53]. Our substrate has $x = 0.3$ Al content, thus, the estimated contact angle is a few grades larger than 50°.

3.2. Crystallization process

First, the curved surface droplets are formed, then the monocrystalline outer shell develops due to the adsorbate effect. The monocrystalline feature is verified by the spotty RHEED image (Fig. 1C). As a third step, the process of crystallization takes place, showing a sign of the crystallographic planes inside the QD. Here, the timing of the process of RHEED sequence and the duration of each RHEED stages are also relevant. For many seconds, the spotty stage (Fig. 1C) remains