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Some aspects to the understanding of the droplet epitaxial nano-hole formation

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ABSTRACT

In this work, the self-assembled GaAs based nano-hole formation prepared by droplet epitaxial technique is discussed. Here, a qualitative explanation is given why thermal solution cannot be observed under droplet edge and can only detected under droplet middle. The thermal etching takes place far from the droplet edge because of its special quantum mechanical state, which causes melting point increase at the droplet edge. Furthermore it is explained, why thermal solution is preferred under the middle of the droplet. Here, we give a lucid interpretation for the nano-hole formation dependence on the arsenic environment. It is evidenced, that the surrounded lobe initiative originates from the remained droplet edge. We give here a qualitative description why we need somewhat ambient arsenic for the process of nano-hole formation. The material transport needs arsenic ambient and not the thermal solution.

1. Introduction

The low-dimensional systems, prepared by molecular beam epitaxy (MBE), has revolutioned the electronic devices both in their potentials and efficiency. Self-assembled quantum dots have garnered a great deal of interest [1] due to quantum confinement and the ability to design nano-structures of unique shapes and sizes thus altering their electronic properties [2]. For a long time, for preparation of zero-dimensional system, the strain-induced technique, based on lattice mismatch, was the only known method [1,3]. On the basis of Koguchi's discovery, a droplet epitaxial technique evolved, giving greater opportunities for the development of the self-assembled nano-structures [4,5]. In this technique, the lattice-mismatch lost its importance. With the usage this new procedure, it is possible to create not only quantum dots (QDs) [6–10] but also quantum rings (QRs) [11–13], double quantum ring (DQRs) [13,14], and nano-holes (NH) [13–17] as well. The electronic structure of these nano-structures depends very strongly on their shape. These quantum objects have the potential to be used in many electronic and optoelectronics devices including photodetectors [18], solar cells [19], light emitting diodes [20], lasers [21], spin memory devices [22], and also quantum computing [23].

Roughly, the droplet epitaxial process consists of two steps: firstly, metal (e.g. Ga) droplets are generated on the crystalline surface in the Volmer-Weber-like growth mode. After them, the crystallization of the droplets takes place and their transformation into e.g. GaAs QDs under arsenic pressure. One advantage of this method is that it does not rely on lattice mismatch strain for nano-structure formation, enabling the formation of nano-structures in previously inaccessible materials systems, such as GaAs/AlGaAs. The further advantage is that droplet epitaxy results in a variety of structures mentioned above. Studies on the droplet epitaxy of lattice mismatched systems have also been undertaken [24–26]. Some of the growth processes are explained, but no general theoretical description is available yet of the underlying growth mechanism.

In this work, we examine the mechanisms for nano-hole formation in the lattice-match AlAs/AlGaAs/GaAs system. Firstly, we give an explanation for the initialization place of the thermal etching of the metallic droplet. After them, we explain the nano-hole formation dependence on the ambient arsenic.

2. Experimental preliminaries

In this part, we refer briefly on three of our earlier experiments, which results in our following explanations are employed. Firstly, we are discussed the status of the metallic droplet surface after its deposition. It is usually, that the status of the MBE grown nano-structures is followed by the reflection high-energy electron diffraction (RHEED). In this case, GaAs QD preparation on AlGaAs surface was carried out. The detailed experiment described in Ref. [27]. At the process beginning, the crystalline AlGaAs surface shows sharp RHEED streaks, which disappear and the diffraction

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picture becomes diffuse during the Ga deposition. The disappearance of the RHEED pattern originates from the appearance of the liquid phase Ga on the surface. In the annealing phase of QD production, the RHEED pattern becomes from diffuse to spotty nearly simultaneously with the opening of arsenic cell. The appeared spotty RHEED pattern originates from the transmission electron diffraction. After the opening of the arsenic cell, a crystalline GaAs shell forms on the surface of the Ga droplet. The electron beam goes through the crystalline GaAs shell layers. It is observed, if there are crystallite formations or droplets on the surface, bulk scattering of the grazing beam can occur and the RHEED pattern may become dominated by spots rather than streaks due to transmission electron diffraction [27]. The existence of such shell configuration has already been observed for In droplets on GaAs [28].

The second experimental result refers to the place of the thermal etching of the metallic droplet. In this case were also prepared GaAs QD on AlGaAs surface at the annealing of 350 °C for 10 min, under arsenic ambient. The sample was investigated by high resolution elemental mapping of transmission electron microscopy. The detailed description of the experiment is in Ref. [29]. The high resolution images clearly show that the QDs contain both Ga and Al. The existence of the Al content is detected at the middle of the QD/substrate interface only. At the edge of the QD, the content is pure GaAs, no Al contamination detected. It is known, that the liquid Ga solves the crystalline AlGaAs. The existence of the Al inside of the GaAs QD originates from the thermal etching followed by mixing. Our experiment clearly presents, that this dissolution and mixing takes place only at the middle of the interface between the Ga droplet and the AlGaAs substrate.

The third cited experiment is concerned to the elemental mapping of the GaAs filled nano-hole created on AlAs surface. The nano-hole was created by Al droplet on AlAs (001) surface under annealing temperature of 600 °C. The substrate consists of thick AlGaAs layer covered by 5.5 nm AlAs layer. The transmission electron microscopically investigation shows V-shaped nano-hole with {111} directed side facets. The hole goes through the covering layer, that is, it is deeper than the AlAs layer thickness. The hole opening is surrounded with a lobed region. The investigation of the elemental mapping shows that the lobe around the hole opening consists of pure AlAs, here, no Ga content detected, however, the bottom of the nano-hole ends inside of the AlGaAs layer. The detailed description of this experiment is to be found in Ref. [30]. The formation of such surrounded lobe has already been observed earlier during etching of AlGaAs with Ga droplets, but its content is not investigated [31].

3. Discussion and results

3.1. Starting point of the thermal solution

For the understanding of the nano-hole formation, the determination of the initial region of the thermal etching has crucial importance. We start from the abovementioned experiment, that is Ga droplet on AlGaAs surface. It is well known from the liquid phase epitaxy, that thermal etching takes place at the interface of the Ga melt and AlGaAs surface [32]. The correlation between meting point and the solubility is also known [33]. The size of our metallic droplet belongs to the nano-range, where the melting point dependence must take into consideration. It is also known, that the melting point lowers with the particle size reduction. This corresponds with the theory of thermodynamics, which states, that small particle should melt at lower temperature than that of the bulk, due to surface effect [34–40]. In bulk, the surface-to-volume ratio is small usually and the curvature of the surface is negligible. Melting of small particles showed a rule of reduction in melting point as approximately 1/r. The ratio breaks down for particles with less than approximately 50 nm diameter (that is around 500 atoms). This is verified theoretically as well as experimentally for different metals [37,38,41–45]. In the upper part of Fig. 1, the solid line depicts the normalized melting curve vs. diameter of the particle. (The normalized melting point means the actual melting point normalized by the bulk ones). It is shown, when the particle size approaches to 50 nm, then the melting point begins to depend very strongly on size. This strong change phenomenon is detected in the case of nano-holes created by Ga droplets with the size of ca. 20 nm. This strong change behaviour provides an interesting anomaly [46]. The melting point problem is more complicated described before because of this parameter depends not only on the particle size but on its shape as well [40].

It is known that the solubility usually increases with the temperature [47]. The melt close or far to the melting temperature has lower or higher solubility, respectively. The experiment clearly proves that the material mixing followed thermal etching happens below the middle of the droplet and not at the edge [29]. The question arises however, that why we observed material mixing (as a consequence of thermal etching) only under droplet middle and not at droplet edges [29]. The theoretical studies of the nano-particles revealed a number of unknown phenomena; some verified experimentally [48]. Let's imagine to divide the metallic nano-droplet as body and edge parts. The part of nano-sized droplet body follows the known melting point decrease on the size [34]. The edge part follows entirely different melting point behaviour. One of those is the fact, that Ga nano-particle, containing less 40 atoms, has their melting points higher than that of the bulk material [48,49]. This over 300 °C melting point are attributed to the strong covalent bonding among the cluster atoms, while the bulk material has weaker covalent–metallic bonding [49,50].

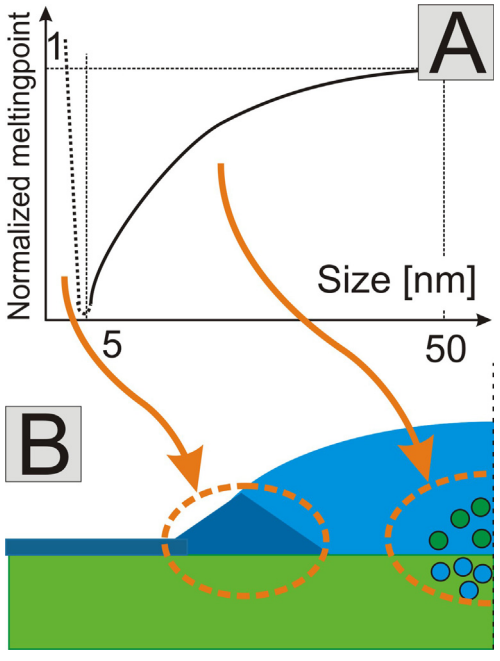

Fig. 1. A: the normalized melting point of the nano-particle. The solid line shows the size dependence between 40 and 500 atom number, while the dotted ones shows it under 40 number of atoms. The curves serve for the qualitative assessment. B: the droplet can divided two regions according to the interaction among the atoms. The dark blue represents the covalent region, the light blue represents the metallic bonding region. The dissolution takes place under light blue region only. The mixing is represented by light bule and green circles. The green colour represents the substrate material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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