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Narrow gap nano-dots growth by droplets heteroepitaxial mode

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ABSTRACT

There is an increasing interest in Quantum Dot (QD) structures for a plethora of applications, including optoelectronic devices, quantum information processing and energy harvesting. Over the last few years, self assembled quantum dots have been observed in a wide variety of semiconductor systems. Several methods for self organized dots have been suggested, among them the most common is the Stranski–Krastanov (S–K) growth mode. The S–K growth mode needs a mismatch between the substrate and the dots material. Recently, an alternative approach of growing QD's, has emerged known as the Droplet heteroepitaxial method. This method is potentially not limited to mismatched material systems and is very attractive for growth of binary and more complicated compounds based on low melting point elements. In this work we present a detailed study on the growth mechanisms of the InSb-based droplets quantum dots and show the large versatility of this droplets growth system in achieving different optical properties of the dots system.

1. Introduction

In recent years a large interest is dedicated to quantum dot (QD) structures for studying basic science as well as for applications. Those include optoelectronic devices [1,2], quantum information processing [3,4], and energy harvesting [5,6]. Strain-driven island forming, via the Stransky–Krastenow mechanism [7–9], is a commonly used fabrication method. A more recent technique, Droplet Heteroepitaxial (DHE) [10–12], does not require mismatch strain and is therefore potentially much more versatile in the combination of materials that can be used to form QDs. We will show in this paper that the DHE method of growth is governed by a rich interplay of structural and compositional rearrangements establishing the extraordinary versatility in dot systems and substrates that can be used by this method. The strain and composition changes created in the InSb-based grown dots determine the confinement potential of electrons and holes and thereby strongly affect the electronic and optical properties of the dots [7,13,14].

InSb is a binary semiconductor material with the largest lattice parameter and the smallest bend gap. The relatively big Bohr radius of InSb (64–68 nm) [15,16] can create quantum effects in this material at rather big sizes up to 70–100 nm. Therefore, InSb is a very attractive material for the production of different quantum structures. However, there are several crucial points, which must be undertaken into the calculation with the design of such structures. Moving from a bulk InSb to a dot system, the level ordering can be dramatically altered even in free standing dots, due to the effects of quantum confinement which drives the direct electron levels up in energy and hole levels down in energy in inverse proportion to their respective effective masses. Direct-to-indirect transition in the case of InSb occurs at a "critical" size of about 4.6 nm [17].

Adding strains to the dots/substrate system can drive levels either up or down in energy scale depending on the sign of the deformation potential. Fig. 1 shows calculation results, obtained using NextNano [18,19] simulator for fully strained 10 nm one dimensional $InAs_{1-x}Sb_x$/GaAs quantum system. In this simulation the energy levels are plotted as a function of the Sb concentration x. The $InAs_{1-x}Sb_x$ undergoes a direct to indirect transition at $x = 0.37$ and indirect semiconductor to semimetal at $x = 0.64$. Furthermore it is evident that a change in the composition of quantum structure leads to a change in band gap alignment between the materials of the GaAs substrate and the grown structure.

This large versatility in the InAsSb/GaAs system makes it a plausible system to study and a good candidate to control with the DHE growth mode. At present very little is known about the atomistic mechanism of QDs formation [20–22], especially those formed by droplet epitaxy (DE). In particular, one would like to know what are the detailed structural and compositional characteristics of this

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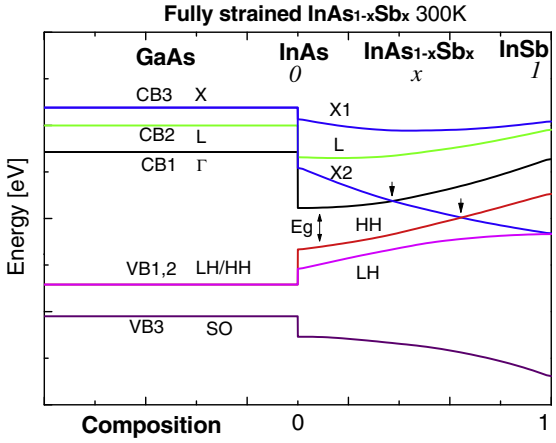

Fig. 1. Calculation of the spacing structure of fully strained 10 nm one dimensional $InAs_{1-x}Sb_x$/GaAs quantum system vs x. The $InAs_{1-x}Sb_x$ undergo a direct to indirect transition at $x = 0.37$ and indirect semiconductor to semimetal at $x = 0.64$.

process as a first step towards the controlled growth of DHE QDs. The DHE method consists two basic stages: the formation of low melting point element nano-droplets on the substrate, and subsequently the exposure of these droplets to the gas phase flow of one or more group IV, V or VI elements. Although the growth process starts with a liquid droplet, the dot will in the end, under proper conditions, be a single crystal atomically registered with the underlying substrate. This method is potentially not limited to mismatched material systems. QD structures with high crystallinity and high-density were demonstrated using the DHE method for the growth of GaAs/GaAs [23], GaAs/AlGaAs [24], GaN/AlGaN [25], InGaAs/GaAs [26], InSb/CdTe [27], InAs/GaAs [28] and InSb on various substrates [11].

The factors governing the DHE nano-dots properties were studied by our group using several methods, while comparing the effects of growth conditions, substrate lattice mismatch and substrate chemical composition [11,21,29,30]. These methods which include the Peak Pairs Algorithm (PPA) [29], Kelvin Probe Force Microscopy (KPFM) [21,29] and the new X-ray diffraction Coherent Bragg Rod Analysis method (COBRA) [30], made it possible to obtain information about the local variations in the substrate-nano-dots system with sub-nano resolution, and to map the strain and composition distribution in grown structures as well as to understand the growth dynamics. The results indicate that the DHE mode is a promising flexible technique for growing InSb and InAsSb nanoscale structures on different substrates. The shapes and density of the final structures are very sensitive to the growth conditions illustrating that this growth mode is more complicated but gives a wide variety of control parameters. The best results in terms of size control and dots density were obtained on As-based substrates, indicating that the surface energy of the substrate plays an important role in this growth mode. The effect of lattice mismatch on the dots size and density is less significant than the substrate surface chemistry. Pre-growth treatment of substrates surfaces by As-source lead to high dots density even on homoepitaxial material system (InSb on InSb) and on amorphous SiO_2, or Spin on Glass (SOG) surfaces. Optical measurements proved that the growth flexibility enables to cover the entire mid-wave atmospheric window [11].

2. Growth model of the DHE InSb-based dots

The deposition of the dots was carried out in a vertical Metalorganic Vapor Phase Epitaxy reactor. In the first stage of the growth indium nano-droplets were formed by supplying of 150 cc of trimethylindium (TMIn) for 2 s to the growth reactor at 410 °C. The rotation speed was 200 rpm and reactor pressure of 76 torr. After the In droplets formation the temperature was decrease to 350 °C. Using the same rotation speed the droplets were exposed to 45 cc trimethylantimony (TMSb) for 5 min for forming final structure. Size, shape and density of droplets formed on the substrates surfaces were found to be very sensitive to the type of the substrate and the growth parameters. Those include temperature of the substrate, susceptor rotation speed and pre-growth exposure of the substrates surfaces to different metalorganic sources.

It is well known, that during exposure of the substrate surface to different elements, these elements are absorbed on the surface and can change the surface energy. Fig. 2 presents the pre-growth treatment influence on quantum dots growth on different substrates. The InSb dots were grown subsequent to supplying of 5 cc TMSb flow for Sb–, and 50 cc flow of tertiarybutylarsine (TBA) for As-pre-growth treatment. We have used GaSb, InSb and amorphous glass substrates, prepared using spin on glass (SOG) solution on silicon. It is interesting to note that short time pre-growth treatment using TBA flow yields high-density ($\sim 10^{11}$ cm^{-2}) InSb nano-dots formation even on the SOG surface (Fig. 2f).

As explained below the presence of liquid metal droplets on the substrate surface, in the first stage of growth, makes the DHE growth very different from other growth techniques. The main difference is the absence of the match/mismatch conception due to solid-liquid interface. In DHE the surface energy play the most critical role in forming of final nano-structures. The density of the obtained nano-structures mostly depends on the number of sub-nano nucleation centers on substrate surface, which in turn is depended on surface reconstruction.

Fig. 3a shows an AFM picture of dense InSb dots grown on GaAs. The height of the dots varies between 3 and 7 nm and the width is changing from 10 to 30 nm. The QD density inferred from the AFM measurements is higher than 10^{10} cm^{-2}. The actual shape of the dots is revealed by Gentle Beam mode on 65° tilted samples using high resolution SEM. All dots have an oval-like shape with a contact angle of approximately 120° [30]. After adding a 70 nm GaAs cap layer, grown at 450 °C by supplying trimethylgalium (TMGa) and TBA for 15 min (Fig. 3b) the dots can be realized at the same density on top of the cap layer (Fig. 3c).

2.1. Pre-growth surface treatment

Adding all experimental data received at the present research allows reconstructing the process of DHE QDs growth and shedding new light on the mechanisms that govern the basic stages of growth.

The first stage of growth which is critical for the DHE growth mode is the pre-growth treatment. In this stage the density and sizes of dots are controlled by using TBA as an As-source or TMSb as a Sb-source before starting the growth. With As treatment the dots grow in high-density, while they are well separated using Sb pretreatment. Fig. 4 is a schematic illustration of the pre-growth treatment stage processes. The GaAs surface changes during pre-growth treatment stage with As- (Fig. 4a) or Sb-sources (Fig. 4b) correspondingly. In this diagram the small squares represent the GaAs crystalline cells, where the surface is assumed to be As-rich with available open bonds. During both these treatments, V-group sources undergo thermal decomposition and create the As- or Sb-reached GaAs surface. This process is followed by the motion of the group V-atoms on the surface and desorption of group V-atoms from the substrate surface, closing the vacancies on the surface. After the treatment stage is finished, group III clusters formation can happen especially in the case of As-treated surface (Fig. 4c).