# Growth and Raman spectra of GaSb quantum dots in GaAs matrices by liquid phase epitaxy

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The self-assembled type-II GaSb quantum dots (QDs) are successfully grown on semi-insulting GaAs (100) matrix by liquid phase epitaxy technique. The topography of QDs with high growth temperature is characterized by atomic force microscopy (AFM). The cap layer, which is needed for the device fabrication, is obtained for only some tens of nanometers. The non-resonant Raman spectra are applied to investigate the GaSb-like optical phonons localized in the QDs and to confirm convincingly the existence of GaSb QDs.

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Comparing with thin films or bulk materials, the design of low dimension materials plays an increasingly important role in the electronic information industry for its miniaturization of structure. Especially for atomic-like quantum dots (QDs) materials, ever since the first self-assembled QDs have been grown using molecular beam epitaxy (MBE)[1]. QDs have received a great deal of attentions for their potential possible applications over the past two decades, especially in devices, such as long lifetime of carrier for charge storage devices[2], high efficiency for semiconductor laser[3], and higher detectivity and responsivity of QD infrared photodetector[4].

Most researches and applications developing on III-V semiconductor QDs have been focused on the InAs/GaAs material system. The GaSb QDs on GaAs matrix, however, are exhibiting a staggered type-II band alignment. Holes in this band structure have strong confinement in QDs, while electrons are very weakly localized by coulomb binding between the buffer layer and barrier layer. The GaSb/GaAs QDs system, thereby, is promising for both fundamental physical effects and novel devices[5]. For example, this system, which supplies a wide barrier choice for GaAs, has provided an alternate choice for the fabrication of infrared light-emitting devices (LEDs). The GaSb QDs structure has high quantum efficiency for the solar cell, especially for the normal incidence. First data for GaSb QDs on GaAs substrate had been obtained using MBE[6]. Their group conducted QDs growth and optical analysis, and applied increasing excitation energy of photoluminescence (PL) to confirm the GaSb/GaAs QDs system type-II band alignment by observation blueshift of the QDs luminescence.

Nevertheless, the majority of GaSb/GaAs QDs systems are grown by MBE[7−9] and MOCVD[2,5,10,11]. As is well known, the epitaxial layer with high quality can be achieved by liquid phase epitaxy (LPE) technique for its near-equilibrium conditions in contrast to other conventional thin film growth techniques, such as MBE or MOCVD. So far, there is absent of related research domestic and overseas by LPE growth for the unique GaSb QDs system except that our group cooperating with Krier in lancaster university shares QDs growth report, which is concentrated on the growth of QDs with contact time more than 4 ms[12].

But the growth of QDs[13] and quantum well (QW)[14] by LPE is upper limit of that to grow ultra-thin layers. The thickness of an epitaxial layer, however, chiefly relies on the difference of the solubility at the initial and final growth temperature, the cooling rate, growth times, volume of the solvent, and undercooling degree, etc. Therefore, there are several solutions that little amount deposition is possible by shortening contact time (in the order of magnitude of 1 ms) when the substrate meet liquid phase solution, or growing under low temperature (low growth rate), or controlling a very thin layer of liquid phase (height of volume is from 200 to 3 000 $\mu$m). QDs would be grown successfully and QW layer with thickness of tens or hundreds of angstroms could be come true[15].

In this letter, we investigate the growth and Raman spectra of GaSb QDs on semi-insulating (100) GaAs matrix in the Stranski–Krastanov (SK) growth mode[16] by modified LPE technique under purified hydrogen atmosphere. The SK growth mode, which is distinguished from Volmer–Weber (VW) mode[17] to Frank–van der Merwe (FM) mode[18] is driven for QDs formation by the energy benefit from elastic relaxation of strain overcoming energy cost of augmented surface area[19]. The lattice mismatch of GaSb/GaAs is up to 7.8%. The large misfit is benefit for the self-organized GaSb island formation. The samples are successfully grown by the combination of thin layer of liquid solution and contact time of a few milliseconds using rapid slider driven by Copley linear motor. With ramp cooling rate of 0.2 °C/min and 20 degrees of undercooling by super cooling method, using the height of 2 548 $\mu$m for liquid phase volume, the specimens labeled 59#, 49#, 61#, and 62# are first grown GaAs buffer at 580 °C with contact time of 180 s, then, short contacted with melt solution for QDs of 10, 6, 4, and

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2 ms, respectively. Two types of samples are prepared for Raman analysis. Some are the QDs specimens of exposed surface. The others are with cap layer, labeled 49#-2 and 62#-2 grown GaAs cap at 510 °C with the same ramp cooling rate and supercooling degrees adopting the growth times 1 and 8 min, respectively. The topography was measured by means of atomic force microscopy (AFM) (NT-MDT, NTEGRA Spectra, Russia). The optical modes of QDs system are investigated by the Raman scattering spectra (NT-MDT, NTEGRA Spectra, Russia). The exciting radiation is 532.8-nm line of laser, and grating is 1 800 G/mm. The exciting power is kept at 3 mW with integral time of 90 s.

As zero dimensional semiconductor structures, QDs are nanoscopic. The size of the QDs is smaller than the deBroglie-wavelength of the charge carrier or smaller than the Bohr radius of the exciton. Because of quantum confinement effect coming from three dimensional size effect, energy level for hole, whose physical properties different from that of bulk semiconductor considerably, will split partially and be kicked out away from potential well. As we know, the de Broglie wavelength $\lambda$ is

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m^* K_B T}}, \tag{1}$$

where $h$, $p$, and $K_B$ are the Planck's constant, momentum, and Boltzmann constant, respectively. From Eq. (1) we obtain $\lambda$, which depends on the effective mass of charge carrier $m^*$ and the temperature $T$. As shown in Fig. 1 we get the curve under the assumption that QDs share the same effect mass with bulk materials.

At ambient temperature the $\lambda$ is 32 nm for light hole of GaSb material, but only 13 nm for heavy hole of GaSb from Fig. 1. By comparison with GaAs charge carrier, we know that the electron and light hole of GaSb share higher de Broglie wavelength except the heavy hole. Thus, GaSb-based nanostructures have typical sizes of some tens of nanometers or below.

Figure 2 presents four AFM images. The round QDs confirm the self-assembled growth under the SK mode. From Fig. 2 we can be directly conscious that medium contact time is benefit for the uniformity. By AFM we can analyze growth process of QDs. The extracted height, width, width-to-height, and density of QDs are shown in Fig. 3.

In Fig. 3, with step by step increasing the contact time from 2 ms, the heights of QDs are increasing, and

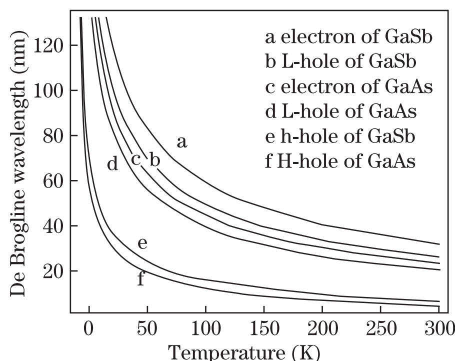


Fig. 1. De Broglie wavelength versus temperature.

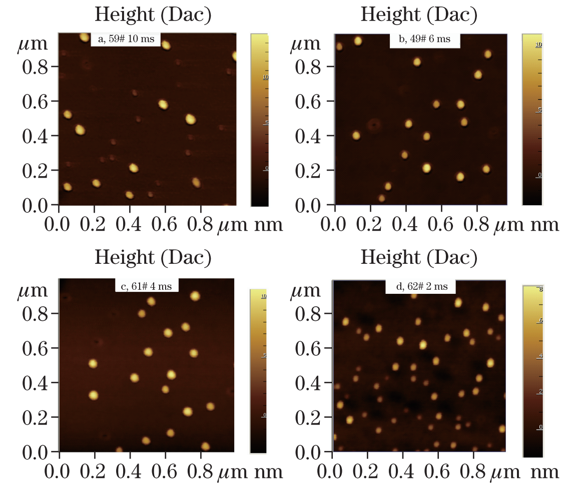


Fig. 2. AFM images for 1 $\mu m^2$.

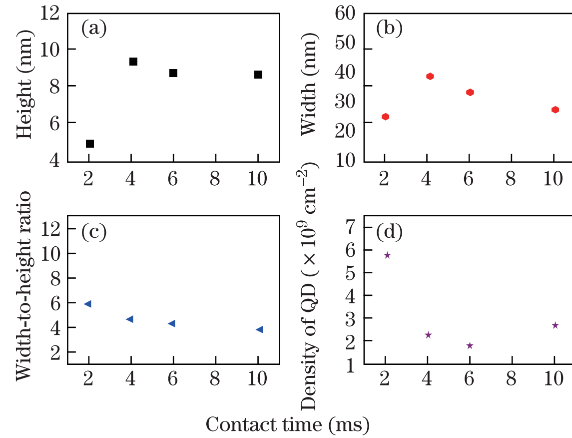


Fig. 3. Contact time versus (a) height of QDs; (b) width of QDs; (c) width-to-height ratio; (d) density of QDs.

then keep almost stabilization. In our experiment the maximal height of GaSb QDs is up to 9.3 nm. However, the width of QDs augment before it reduce, which is depending on the thermodynamics of atom diffusion and incorporation. The range of average width is from 30 to 43 nm. In Fig. 3(c), with increasing the contact time, the width-to-height ratio is linear-like decreasing. That is to say that QDs are prone to grow higher rather than wider with increasing contact time. The density of QDs is reducing before augmenting. At 2 ms, the height and width is small. But density is high, up to $5.7\times10^9$ cm$^{-2}$. Along with increasing contact time, the height and width are increasing, but the density is reducing because of the mergence of QDs. Further increasing the contact time, the height and width are reducing, but the density of QDs is adding for the more deposition and diffusion of GaSb atoms. The variational processes of height and width of QDs are evidence for the growth dynamics of QDs.

The growth condition of sample 47#-2 is the same as the buried QDs except from the contact time of 3 min for growth of GaAs cap layer. The thickness of cap layer for 47#-2 is about 20 nm as presented in Fig. 4. The effect of cap layer is rather abundant and needed for devices fabrication to confine hole charge carrier[20], and the incomplete covering layer presents the successfully growth of cap layer. In addition, a big round pit appears

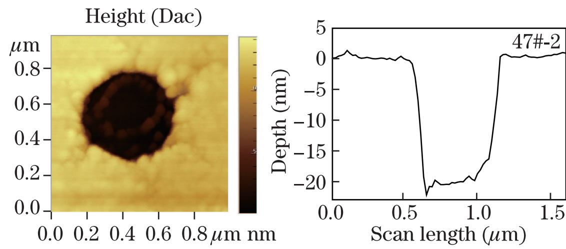


Fig. 4. Sketch of the capping layer by AFM.

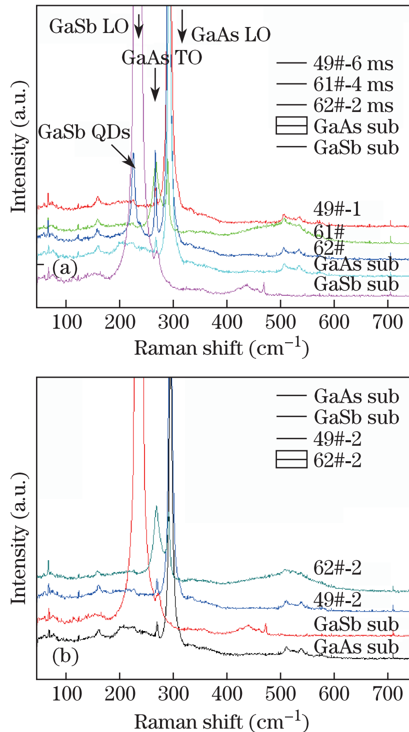


Fig. 5. Raman spectra of (a) QDs unencapsulated and (b) QDs encapsulated.

in the center of Fig. 4, and there are a circle of QDs in the pit. The phenomenon of pit enclosed a circle of QDs should be related with bigger surface energy originating from the circle of QDs, which depresses the deposition and diffusion of GaAs atoms to form the cap layer.

From Fig. 5, under the non-resonant conditions, as expected, we observe longitudinal optical (LO) mode and transverse optical (TO) mode of GaAs, which present at 291 and 267 $cm^{-1}$, respectively[21]. The samples of GaAs sub and GaSb sub are the virgin substrate for referring peak position. The specimen 62# of 2 ms shows the third incisive peak at 226 $cm^{-1}$, and other QDs unencapsulated are presented rather week peak locating at the 226 $cm^{-1}$. The optical phonon localized in the Γ point of brillouin zone could be observed by Raman diffusion spectra, but the acoustic phonon is not allowed. Ways of research are possible only if by neutron scattering or brillouin zone scattering. The peak of 226 $cm^{-1}$ is longitudinal acoustic (LA) mode of GaAs at X point, but it is not possible for Raman scattering. In addition, film or bulk GaSb have the energies the LO (238 $cm^{-1}$) and TO (228 $cm^{-1}$)[22], so the peak of 226 $cm^{-1}$ should be the vibrational excitation for the GaSb QDs, which is agrees with the findings of Bennett[23]. The fabrication of capping layer is design for Raman analysis to avoid the weak scattering from a single layer of dots, and the penetration depth of Raman laser for 520 nm is few tens of nanometers for GaAs materials. But the specimens of QDs encapsulated present very weak QDs signal in 226 $cm^{-1}$ or absent in the strict sense.

The vibration phonons in bulk GaSbAs alloys present two-mode behavior, and have a GaAs-like mode at an energy 243 $cm^{-1}$ for small As concentration[23]. So it can be concluded that the QDs are relatively pure GaSb since we can find no such mode from the curve of Raman. Raman spectra support a method to identify the chemical composition of the QDs. Besides Raman analysis, these are little known for the chemical composition of the QDs. In addition, the TO mode is prohibited for the (100) oriented substrate for the non-zero polarization selection rule. But the TO mode is presented. The reason may be the deviation of matrix orientation for only small angle.

In conclusion, we give the growth and Raman spectra of GaSb QDs in GaAs matrix by LPE. The serial of QDs samples with short contact time are detailedly investigated by the AFM. The growth window for QDs is investigated, and it is presented that the growth dynamics of QDs evolve from small QDs to big ones. The cap layer with few tens of nanometers is come true by LPE. Applied Raman spectra, the GaSb QDs are confirmed, and the pure chemical composition of GaSb QDs is identified.

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