Nucleation of GaSb on GaAs (001) by low pressure metal–organic chemical vapor deposition*

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The initial growth stage of GaSb on GaAs (001) by low pressure metal–organic chemical vapor deposition (MOCVD) is investigated. The dependence of the nucleation on growth temperature, growth pressure, and vapor V/III ratio is studied by means of atomic force microscopy. The nucleation characteristics include the island density, size, and size uniformity distribution. The nucleation mechanism is discussed by the effects of growth temperature, growth pressure, and vapor V/III ratio on the density, size, and size uniformity of GaSb islands. With the growth temperature increasing from 500 °C to 610 °C and the growth pressure increasing from 50 mbar to 1000 mbar (1 mbar = 10^5 Pa), the island density first increases and then decreases; with the V/III ratio increasing from 0.5 to 3, the trend is contrary.

Keywords: MOCVD, GaSb, nucleation

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1. Introduction

Sb-based compound semiconductors have attracted a lot of attention in recent years. These semiconductors are expected to be used to fabricate high-performance long-wavelength devices such as infrared lasers, infrared detectors, solar cells, and quantum dot (QD) memory devices.[1–5] In recent years, GaSb heteroepitaxy has made great advances. GaSb and many group III–V semiconductors such as GaAs and InGaAs have the same crystal structure and the heterostructures of GaSb/GaAs (InGaAs) are of type-II band alignment. The spatial separation of electrons from holes in type-II structures results in a long exciton lifetime. The structures could grow on GaAs, InP, and other substrates.[6–12]

The lattice constant of GaAs is ∼5.6 Å, and of GaSb it is ∼6.1 Å. Because the lattice mismatch between GaAs and GaSb is ∼8%,[13] epitaxial growth of the GaSb/GaAs heterostructures with a high crystalline quality is difficult. Nucleation is the first stage of the epitaxial process by metal–organic chemical vapor deposition (MOCVD). However, few reports on the nucleation mechanisms of GaSb on GaAs prepared by MOCVD are available from the literature.[14] It is important to study the nucleation of GaSb on GaAs substrate for growing high quality heterojunctions and GaSb QDs.

In this paper, the initial growth stage of GaSb on GaAs (001) grown by low pressure metal–organic chemical vapor deposition (LP-MOCVD) is studied. The effects of growth parameters on GaSb nucleation are discussed in detail.

2. Experiments

The samples were grown by LP-MOCVD on semi-insulating GaAs (001) substrates. The horizontal reactor is equipped with an RF-heated graphite susceptor. Trimethylgallium (TMGa) and triethylantimony (TESb) were used as Ga and Sb sources, respectively. Purified hydrogen gas was used as a carrier gas. Thermal cleaning was performed to remove other contaminants by keeping the substrates at a temperature of 430 °C for 15 min. The total gas flow was 6.5 slm. The growth time for all samples was 5 s. TESb flow was input in the reactor before the growth and afterwards as a protection for restraining the volatilization of V group elements.

Three groups of experiments were designed. Each group contained five runs. Group 1 considered the growth temperature varying from 500 °C to 610 °C. Group 2 considered growth pressure varying from 50 mbar to 1000 mbar. Group 3 was about varying the V/III ratio from 0.5 to 3.

The GaSb islands were characterized by the Dimension®Icon Atomic Force Microscope (AFM) system (Bruker AXS Inc.). The AFM is performed in noncontact mode at a resonance frequency of 300 kHz. The minimum radius of curvature of AFM is 1 nm. The average size and the density data of GaSb islands were analyzed by NanoScope Analysis software.

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3. Results and discussion

3.1. Dependence of GaSb nucleation on growth temperature

Figure 1 shows AFM images of GaSb morphologies on GaAs substrates for different temperatures. The lattice mismatch between GaSb and GaAs is ∼8%. The GaSb nuclei deposited on GaAs substrates in the initial stage of the growth change into small islands by a self-organized mechanism.[8,13,15,16] As shown in Fig. 1, the islands could be observed on all samples. The epitaxial layer nominal thickness values and the growth rates of the five samples above are shown in Table 1.

Table 1. The nominal thickness values and the growth rates of the GaSb layers for different growth temperatures.

Sample	Growth time/s	Growth temperature/°C	Nominal thickness/ML	Growth rate/(ML/s)
a	5	500	28.1	5.6
b	5	530	31.5	6.3
c	5	550	43.3	8.7
d	5	580	38.8	7.8
e	5	610	47.0	9.4

The variation of GaSb island density is shown in Fig. 2. The island density first increases and then decreases with the growth temperature increasing from 500 °C to 610 °C. The samples with the highest GaSb island density of $4.7 \times 10^9/\text{cm}^2$ and the lowest one of $1.1 \times 10^9/\text{cm}^2$ are grown at 550 °C and 610 °C, respectively.

The decomposition rates of TMGa are ∼30% at 500 °C and ∼50% at 550 °C respectively. The decomposition rate of TESb is more than 50% at 500 °C, higher than that of TMGa. The decomposition rate of the organometallic source is lower at low temperatures, causing a small number of reaction atoms, especially Ga atoms, to participate in the reaction. According to Liu and Zhu,[17] from fluid mechanics, the nucleation rate equation is given as

$$J = Z\omega C(i^*), \tag{1}$$

where Z is the Zeldovitch factor, ω is the frequency at which a critical cluster can adsorb one atom then transform into a stable nuclei, and $C(i^*)$ is the concentration of the critical cluster. i is the number of atoms contained in one critical cluster. i decreases with temperature decreasing, however, i is usually less than 7 for metal vapor deposition at very low temperatures, so i changes slightly. $C(i^*)$ is mainly dependent on the concentration of reaction atoms. Obviously, ω is also related to the concentration of reaction atoms. Hence, low temperature leads to the decrease of the island density.

This effect is more obvious for low temperatures less than 550 °C. It causes the density of GaSb islands to decrease. According to the report of Kotaro Zaima *et al.*,[18] 540 °C was an appropriate temperature for improving the crystalline quality of GaSb film on GaAs. It is inferred that atomic clusters deposited on GaAs substrate cause the crystalline quality to decrease and induces polycrystalline GaSb to form. The effect plays a dominant role at temperatures lower than 550 °C.

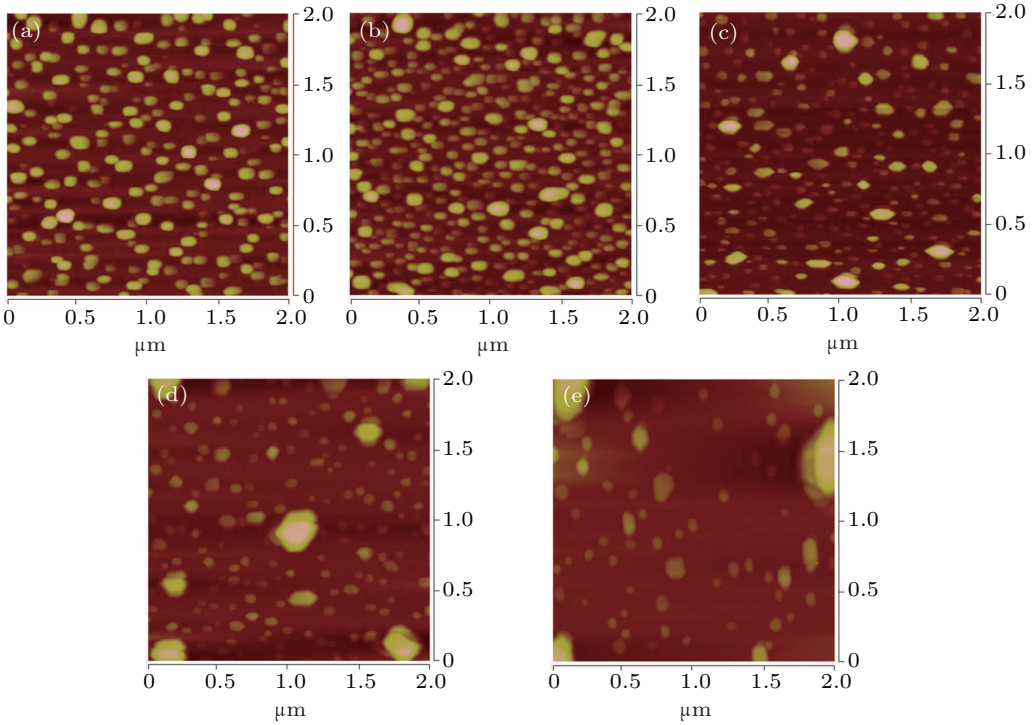


Fig. 1. (color online) AFM images of GaSb morphologies on GaAs substrates for different temperatures: (a) 500 °C, (b) 530 °C, (c) 550 °C, (d) 580 °C, and (e) 610 °C, respectively.

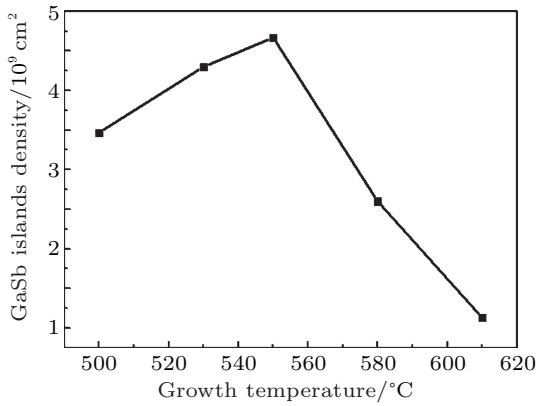


Fig. 2. Dependence of GaSb island density on growth temperature.

For growth temperatures higher than 550 °C, the migration length of adatoms increases with temperature increasing.[19] A longer migration length leads to a lower density of GaSb islands as more adatoms can go to one point on the substrate. Further, the desorption effect is enhanced with increasing the temperature. The mean residence time in which atoms are adsorbed on substrate, τ_A, can be given by the De Boer relation:

$$\tau_A = \tau_0 \, e^{\Delta H_d / KT}, \tag{2}$$

where τ_0 is the reciprocal of the shake frequency of the adatoms, and ΔH_d is the desorption heat.[17] Hence, τ_A decreases with temperature increasing. The flow of carrier gas is not considered in this case. From the ideal gas equation

$$PV = nRT, \tag{3}$$

it follows that T is inversely proportional to n when the PV is kept constant. It indicates that the organometallic source concentration becomes lower in the reactor with increasing temperature. Suppose that the volume of reactor V keeps unchanged in the growth process, the velocity (v) of the gas flowing through the surface of GaAs substrate is calculated as follows. Let r_f and t be the total gas flow in the reactor and the average time for a molecule to stay in the reactor, then the mole rate of the total gas flow at room temperature will be given as

$$r_m = \frac{r_f \times 273.15 \text{ K}}{22.4 \text{ L/mol} \times 300 \text{ K}}, \tag{4}$$

the total number of molecules of substance of gas in the reactor can be given by

$$n = \frac{PV}{RT}. \tag{5}$$

Hence,

$$t = \frac{n}{r_m} = \frac{P}{T}\frac{V}{Rr_m}. \tag{6}$$

The average velocity v with which each molecule passes through the substrate is proportional to $1/t$, i.e.,

$$v = a\frac{1}{t} = a\frac{T}{P}\frac{Rr_m}{V}. \tag{7}$$

So

$$\begin{cases} v \propto T, \\ v \propto \dfrac{1}{P}. \end{cases} \tag{8}$$

From this formula, the total reaction number of the molecules is unchanged, but molecules pass through the substrate at a faster velocity with increasing temperature. The velocity has a 13% increase in a temperature range from 500 °C to 610 °C. So increasing temperature brings about a lower deposition. This effect is not obvious for a very fast deposition. In the case of pressure variation, low pressure causes the velocity of carrier gas to greatly change. The change will be discussed in detail in the next session. Moreover, according to fluid mechanics, gas viscosity μ can be calculated from the Satran formula:

$$\frac{\mu}{\mu_0} = \left(\frac{T}{T_0}\right)^{3/2} \frac{(T_0 + B)}{(T + B)}, \tag{9}$$

where T_0 is the reference temperature, μ_0 is the corresponding viscosity, B is a constant related to the gas species. Gas viscosity increases with increasing temperature. The increase of viscosity leads to a lower GaSb island density since the adsorption becomes difficult. High temperatures result in the 'Ostwald-ripening' as well.[20] Due to the fusion within the GaSb islands, the density of islands decreases.

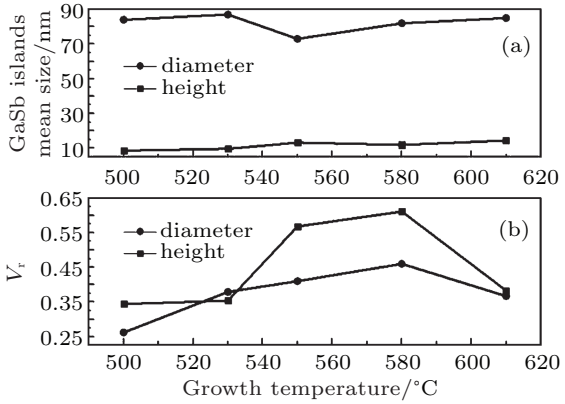


Fig. 3. (a) Mean size of GaSb islands versus growth temperature. (b) Size uniformity of GaSb islands versus growth temperature.

The dependences of the mean size of GaSb islands and the size uniformity on growth temperature are shown in Figs. 3(a) and 3(b) respectively. V_r is the ratio of island size variance to island mean size for presenting the size uniformity of GaSb islands. The mean diameter is minimum for the islands with a maximum density as shown in Fig. 3(a). This inference matches perfectly to the cases of the pressure (shown in Figs. 5

and 6) and the V/III ratio (shown in Figs. 8 and 9). Hence, through influencing the density, growth temperature affects the distribution of island diameter indirectly. The island height increases slightly with temperature increasing. It shows that the increase of temperature leads to the decrease of the uniformity of GaSb island distribution in the aggregate. At a temperature of 610 °C, the uniformity improves a little with adequate ripening.

3.2. Dependence of nucleation on the growth pressure

Figure 4 shows AFM images of the morphologies of GaSb islands on GaAs substrates for different reaction pressures. The epitaxial layer nominal thickness values and the growth rates of the five samples above are shown in Table 2.

Table 2. The nominal thickness values and the growth rates of the GaSb layers for different pressures.

Sample	Growth time/s	Growth pressure/mbar	Nominal thickness/ML	Growth rate/(ML/S)
a	5	50	49.8	10.0
b	5	100	37.7	7.5
c	5	300	32.1	6.4
d	5	600	28.2	5.6
e	5	1000	35.4	7.1

The density with quasi-parabola distribution changes with pressure varying from 50 mbar to 1000 mbar. The sample with the highest GaSb island density of $\sim 4.2 \times 10^9/\mathrm{cm}^2$ is grown at 300 mbar, and the lowest one of about $1.2 \times 10^9/\mathrm{cm}^2$ is grown at 50 mbar. The dependence of GaSb island density on growth pressure is shown in Fig. 5.

Lower nucleus density under lower growth pressures less than 300 mbar can be mainly ascribed to the lower concentration of organometallic source. Lower concentrations of organometallic sources cause less atoms to participate in the reaction. The explanations for the effects are just like those for the case of low temperatures discussed above, therefore here it is not discussed any further. Another reason is that the desorption effect becomes stronger as the growth pressure approaches the vacuum. In addition, due to formula (4), $v \propto 1/P$, the velocity with which a molecule passes through the substrate at 50 mbar is six times that at 300 mbar. The lower nucleus density can also be ascribed to this reason. On the contrary, when pressure increases to higher than 300 mbar, with the reduction of molecular mean free path, the collisions between atoms become more frequent. This cause leads to a more obvious cohesion effect before Ga and Sb atoms are adsorbed. As a result, there are many more clusters and stable nuclei in the vapor. In a deposition process, when the number of adatoms is far more than that of ad-clusters, the distribution of the free energy of clusters can be given as

$$\Delta G_{\mathrm{g}} = -KT \ln\left(\frac{n_0}{n_{\mathrm{s}}}\right), \tag{10}$$

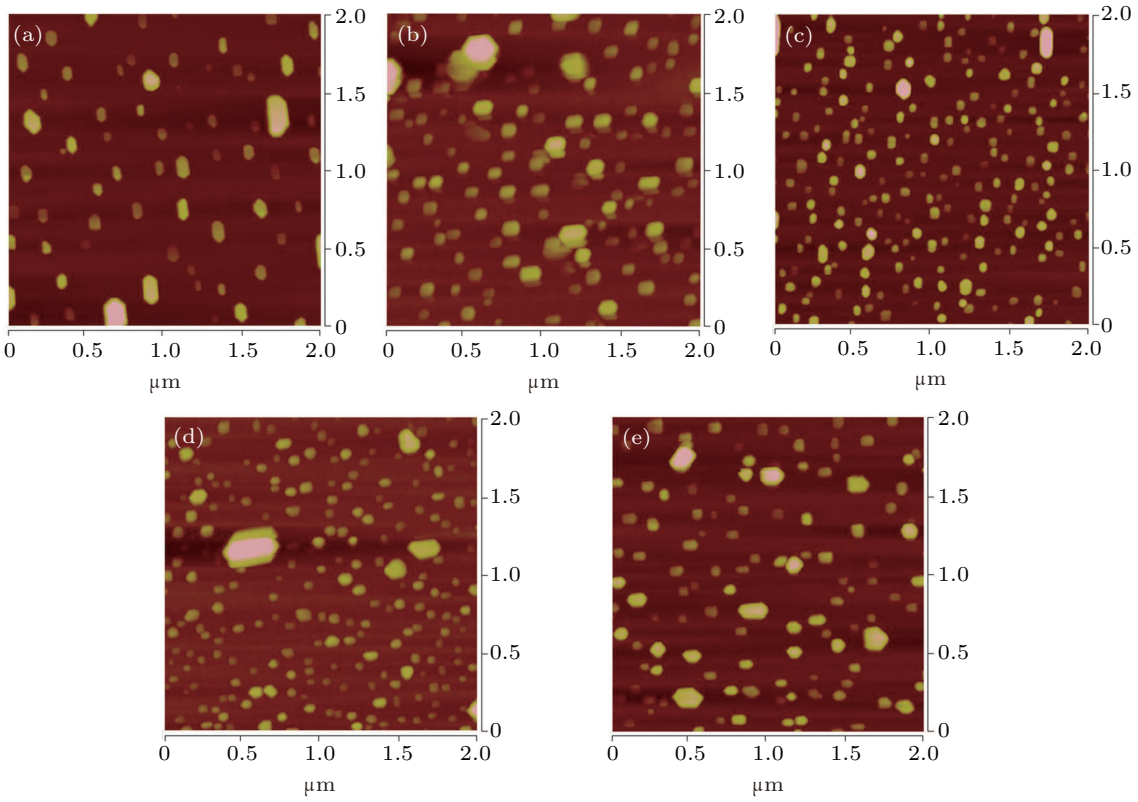


Fig. 4. (color online) AFM images of GaSb morphologies on GaAs substrates for different pressures: (a) 50 mbar, (b) 100 mbar, (c) 300 mbar, (d) 600 mbar, and (e) 1000 mbar, respectively.

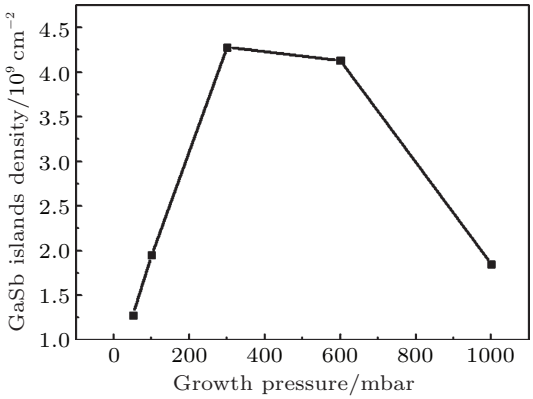


Fig. 5. Density of GaSb islands versus growth pressure.

where n_0 and n_s are the total lattice number on the substrate and the lattice number which can be occupied by clusters, respectively.[17] For large clusters, n_s is smaller; then ΔG_g decreases. In other words, the probability for a large cluster to deposit on a substrate is less than that for a small cluster or an atom. Hence, a sufficiently high pressure will lead to a lower density of GaSb islands.

The dependence of the mean size of the GaSb islands on the growth pressure is shown in Fig. 6(a), and that of the size uniformity is shown in Fig. 6(b). The growth pressure affects the distribution of island diameters indirectly. Due to a higher density, islands have smaller sizes: $\sim$ 72 nm in diameter and $\sim$ 9 nm in height, for growth pressure ranging from 300 mbar to 600 mbar. The mean height of GaSb islands varies slightly. The sample grown at a pressure of 300 mbar is more uniform than at the other pressures.

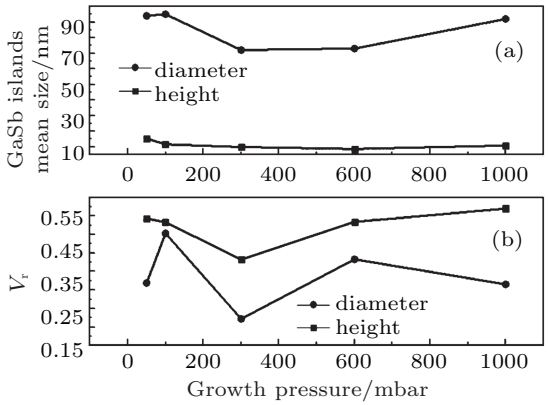


Fig. 6. Variations of (a) GaSb island mean size and (b) GaSb island size uniformity with growth pressure.

3.3. Dependence of nucleation on the vapor V/III ratio

Figure 7 shows AFM images of the morphologies of GaSb islands on GaAs substrate for different V/III ratios. The epitaxial layer nominal thickness values and the growth rates of the five samples above are shown in Table 3.

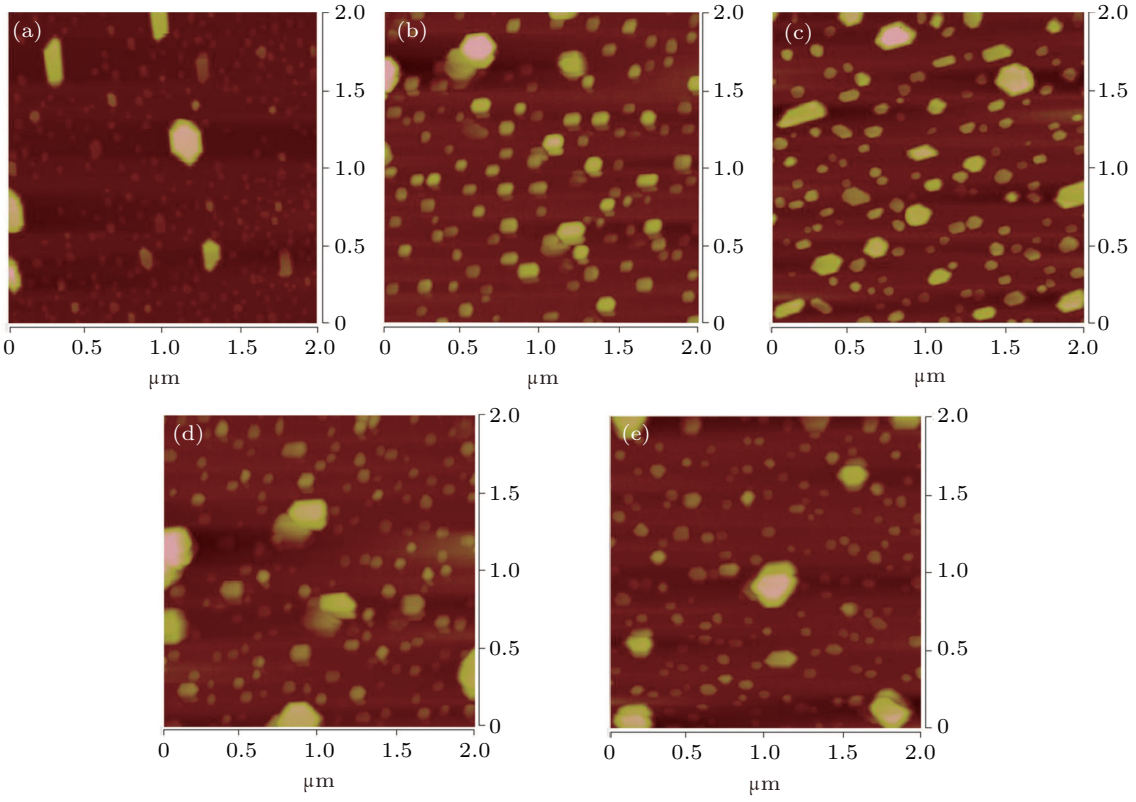


Fig. 7. (color online) AFM images of GaSb morphologies on GaAs substrates for different V/III ratios: (a) 0.5, (b) 0.75, (c) 1, (d) 2, and (e) 3, respectively.

Table 3. Epitaxial layer nominal thickness values and the growth rates of the GaSb layers for different V/III ratios.

Sample	Growth time/s	V/III ratio	Nominal thickness/ML	Growth rate/(ML/s)
a	5	0.5	40.1	8.0
b	5	0.75	37.7	7.5
c	5	1	63.2	12.6
d	5	2	37.7	7.5
e	5	3	37.6	7.5

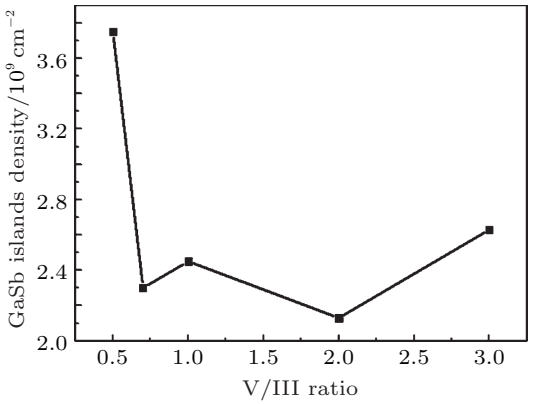


Fig. 8. Effect of V/III ratio on the density of GaSb islands.

The island density changes lightly from 2.13×10^9/cm^2 to 2.63×10^9/cm^2 with the V/III ratio varying from 0.75 to 3, which is shown in Fig. 8. However, island density increases sharply at a V/III ratio of 0.5. Usually, more Sb sources are needed in growth since an element of group V volatilizes easily. So TESb flow is kept before the growth and afterwards as a protection for restraining the volatilization. It leads to an Sb-rich surface of GaAs substrate in the initial growth stage. In addition, with keeping the total mole quantity of TMGa and TESb fixed, for a low V/III ratio of 0.5, a higher density of $\sim 3.75 \times 10^9$/cm^2 is obtained at a higher TMGa concentration. An even lower TMGa proportion brings about the decreasing GaSb island density, but the migration length of Ga atoms on GaAs is longer than that of an Sb atom. Under the influence of a higher Sb concentration, the shorter migration length of Ga atoms leads to a stable density of GaSb islands. Hence, a lower V/III ratio is suited for GaSb QD growth, but highers V/III ratios are necessary for GaSb thin film growth.

The dependences of the mean sizes of GaSb islands and the size uniformity on the V/III ratio are shown in Figs. 9(a) and 9(b), respectively. The GaSb islands with the maximum density come with the minimum base diameter. The mean height of the GaSb islands changes little with V/III ratio, almost in a range of 11 nm–12 nm, except the mean height of $\sim$ 19 nm at V/III = 1. The exception may be attributed to a high utilization coefficient of the organometallic source. Since the V/III ratio matches the stoichiometric ratio of GaSb, the total mole quantity of deposition increases. For the size uniformity of GaSb islands, the best sample is obtained at V/III = 1. The general trend is that the GaSb islands will be more uniform when the V/III ratio is close to the solid stoichiometric ratio of GaSb.

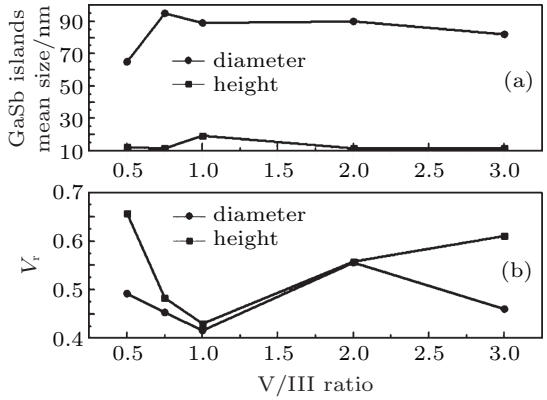


Fig. 9. (a) Mean size and (b) size uniformity of GaSb islands versus V/III ratio.

4. Summary

Under different growth conditions of the GaSb initial growth stage, the effects of growth temperature, reaction pressure, and vapor V/III ratio on the GaSb nucleation on GaAs matrix are investigated by means of AFM. It is found that the dependence of GaSb nucleation on the growth temperature is the most complicated. In the initial growth stage of GaSb on GaAs, the findings are obtained as follows.

The island density first increases and then decreases with increasing temperature or pressure. However, it first decreases and then increases with increasing V/III ratio. The GaSb island diameter decreases as island density increases. The GaSb island height changes slightly with growth temperature, growth pressure, and V/III ratio. The diameter uniformity of GaSb islands is usually better than the height uniformity. Size uniformity increases with decreasing temperature. The GaSb islands are more uniform for the V/III ratio close to the solid stoichiometric ratio of GaSb. The temperature 550 °C is an appropriate temperature for GaSb growth.

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