Molecular beam epitaxial growth of InSb, GaSb, and AlSb nanometer-scale dots on GaAs

Brian R. Bennett,[a] R. Magno, and B. V. Shanabrook
Naval Research Laboratory, Washington, DC 20375-5347

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Thin layers of InSb, GaSb, and AlSb were grown on GaAs substrates by molecular beam epitaxy. Atomic force microscopy was used to examine surface morphology as a function of growth temperature and monolayer coverage. For each material, conditions were found which resulted in Stranski–Krastanov growth with the strain-induced formation of nanometer-scale dots. Relatively uniform distributions of dots form in a temperature window near the congruent sublimation temperature for both InSb and GaSb. In the case of InSb, deposition of 2 monolayers at 430 °C produced a surface with $3\times10^9/\mathrm{cm}^2$ dots with heights of 58±5 Å and diameters of 600±50 Å. [S0003-6951(96)00804-0]

The self-assembly of quantum structures promises to provide a mechanism for producing arrays of quantum wires or quantum dots. Furthermore, with a clever choice of materials that exhibit thermodynamic and kinetic properties that drive the self-assembly process, it may be possible to form ensembles of nearly identical quantum systems. If such a process can be invented, the electronic and optical properties will exhibit little inhomogeneous broadening and should be ideal for use in applications. Although this research is in its embryonic stage, several groups have employed Stranski–Krastanov (SK) growth as a vehicle for producing InAs quantum dots embedded in GaAs.[1–8] In this letter, we report the formation of nanometer-scale dots of InSb, GaSb, and AlSb on GaAs substrates. These structures have potential applications in basic studies of quantum confinement as well as electronic and optical devices. In addition, the study of these systems augments the number of different lattice mismatch and surface energy combinations available in the search for an improved understanding of the growth processes involved.

We grew samples by solid-source molecular beam epitaxy (MBE) on semi-insulating (SI) or n^+GaAs substrates, oriented within 0.1° of (001). First, a GaAs buffer layer, approximately 1 μm thick, was grown at 580 °C. For growth on SI substrates, the GaAs buffer layer was not intentionally doped. For growth on n^+ substrates, the buffer layer was doped with Si at $10^{18}/\mathrm{cm}^3$. Growth was monitored by reflection high-energy electron diffraction (RHEED). During the GaAs buffer growth, the RHEED pattern is a streaky 2×4 reconstruction with no evidence of transmission spots. Before the growth of the dots, a 450 s growth interrupt under an As_4 flux was performed and resulted in sharp diffraction spots along each streak, indicating the formation of large islands. Then, the substrate temperature was reduced, the valve for the arsenic source was closed to minimize As incorporation, and the antimonide layer was grown by migration-enhanced epitaxy with a cation deposition rate of 0.10 monolayers (ML)/s and a V:III flux ratio of approximately 2:1. After deposition of the (In,Ga,Al)Sb monolayers, the sample was held at the growth temperature under an Sb_4 flux for 140 s before cooling. All samples were characterized by atomic force microscopy (AFM) using silicon nitride cantilevers under ambient conditions.

We begin by considering the growth of InSb on GaAs. InSb has the smallest band gap (0.18 eV at 300 K) and largest lattice constant (6.479 Å) of the binary III–V compound semiconductors. Its lattice constant is 15% larger than that of GaAs. During cool-down before the antimonide growth, the RHEED pattern transforms to a $c(4\times4)$. After 1.5–2.0 ML of InSb, chevrons and/or transmission spots appear, indicating three-dimensional growth.

AFM scans of our standard GaAs buffer layer reveal 3 Å monolayer steps with a spacing of a few thousand angstroms. After 1.0 ML of InSb at 400 °C, the surface remains relatively flat (rms roughness ≅1 Å). After 1.5 ML, however, about $5\times10^7/\mathrm{cm}^2$ isolated dots are present, as shown in Fig. 1(a). Typical dot heights and diameters are 40 and 500 Å, respectively.[9] The dots are more numerous after 2.0 ML: density $\cong3\times10^9/\mathrm{cm}^2$, height=53±6 Å, and diameter =500±80 Å [Fig. 1(b)], where the ± values are the standard deviation based upon at least 15 dots. Dots are larger and less uniform after 3.5 ML of InSb: density $\cong6\times10^9/\mathrm{cm}^2$, height =117±34 Å, and diameter =700±110 Å [Fig. 1(c)]. After 4.0 ML (not shown), the density has dropped to $3\times10^8/\mathrm{cm}^2$ and the dimensions are height =208±32 Å, and diameter =1700±300 Å, with somewhat oval rather than circular shapes. The evolution of island size is similar to the InAs/GaAs system.[1] We speculate that misfit dislocations have formed in some of the islands at 3.5 ML, resulting in bigger dots and a larger spread in the size distribution.[10] After 4.0 ML, coalescence has occurred. The growth temperature was 400 °C for all three samples in Fig. 1.

A second set of InSb samples was grown with constant thickness (2.0 ML) and variable temperature. AFM images for growth temperatures of 350, 430, and 460 °C are shown in Fig. 2. Islands are present at 350 and 460 °C, but their sizes and shapes are very irregular. In contrast, the 430 °C sample contains a relatively uniform distribution of dots. The density and size distribution are comparable to the 2.0 ML, 400 °C sample [Fig. 1(b)]: density$\cong3\times10^9/\mathrm{cm}^2$, height

[a]Electronic mail: bennett@bloch.nrl.navy.mil

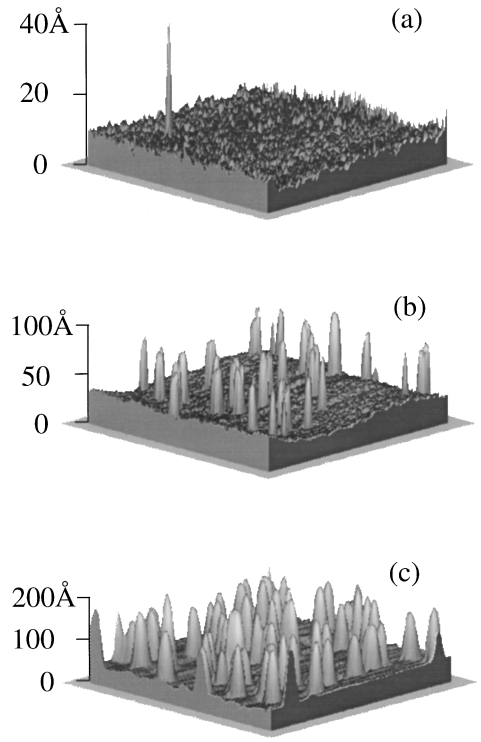

FIG. 1. AFM images (1 μm by 1 μm) of InSb grown on GaAs at 400 °C: (a) 1.5 ML InSb, (b) 2.0 ML InSb, and (c) 3.5 ML InSb.

$=58\pm5$ Å, and diameter $=600\pm50$ Å. We note, however, that dot distributions are not always reproducible. For example, in one case a 2.0 ML, 400 °C InSb growth resulted in dots with an unusual double-peaked shape. The growth conditions were nominally the same as in Fig. 1(b), but perhaps subtle changes in temperature, flux, or GaAs surface morphology could account for the differences.

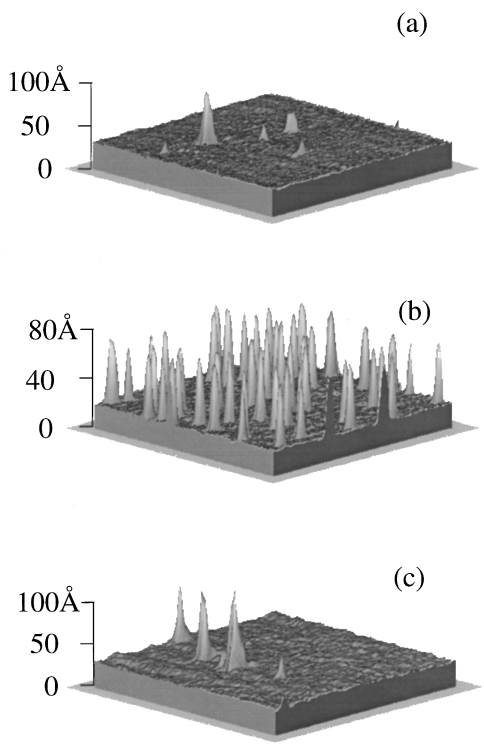

FIG. 2. AFM images (1 μm by 1 μm) of 2.0 ML InSb grown on GaAs: (a) 350 °C, (b) 430 °C, and (c) 460 °C.

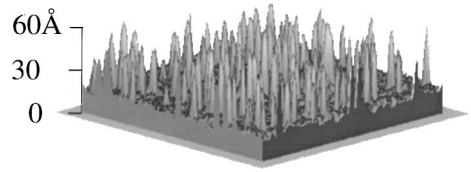

FIG. 3. AFM image (1 μm by 1 μm) of 3.0 ML GaSb grown on GaAs at 460 °C.

The InSb dot heights and diameters after 2.0 ML at 400–430 °C are about a factor of 2 larger than reported values for InAs on GaAs, and the uniformities are comparable.[1–3]. The optimal growth temperature for InSb/GaAs dots is 400–430 °C, compared to about 500 °C for InAs/GaAs. The congruent sublimation temperatures (T_{cs}) are 400 and 500 °C for InSb and InAs, respectively.[11] (We note, however, variation in the reported values of T_{cs}.) Hence, the optimal growth temperatures for nanometer-scale dots are near T_{cs} in both systems. Growth at higher temperatures may not be possible due to desorption. At lower temperatures, atoms deposited on the surface may not have sufficient mobility to reach and incorporate into the dots. If dot formation is limited by growth kinetics, then growth rate and postgrowth annealing time could be important factors. To test this, an additional 2.0 ML InSb sample was grown at 400 °C, but with a 1.0 ML/s growth rate and immediate cooldown after growth. The AFM images (not shown) reveal highly irregular islands.

Nucleation sites also play an important role in the distribution and uniformity of dots. Work in the InAs/GaAs system revealed preferential nucleation of dots at step edges.[2] We grew 2 ML of InSb under conditions which normally produce a uniform distribution of dots: 400 °C, 0.10 ML/s, 140 s postgrowth anneal [as in Fig. 1(b)]. Instead of the normal GaAs buffer layer, however, the InSb was grown on: 1 μm GaAs/1 μm AlSb/0.3 μm GaAs/GaAs(001). The InSb formed a very nonuniform distribution of dots with most dots forming on step edges and surface defects. The nonideal starting surface probably resulted from misfit dislocations induced by the large lattice mismatch between the underlying GaAs and AlSb.

We now address the growth of GaSb and AlSb, materials with lattice constants near 6.1 Å, on GaAs. The surface energy[12] of GaSb is smaller than GaAs and the lattice constant is 7.8% larger. Hence, one might expect growth by the SK mode under certain conditions. We have indeed achieved SK growth and nanometer-scale dots of GaSb on GaAs. For growth temperatures of 460–500 °C, the 2D to 3D transition occurs between 2 and 3 ML. In Fig. 3, we show a 1 μm by 1 μm AFM image for 3.0 ML GaSb grown at 460 °C. The density of dots is about $10^{10}/\mathrm{cm}^2$, with heights of 32 ± 9 Å and diameters of 280 ± 40 Å. The dot dimensions are smaller than InSb and similar to InAs dots on GaAs (6.9% mismatch).[1] A 3 ML growth at 500 °C produced a similar distribution of dots with an average height and diameter of 52 and 350 Å, respectively. No dots were present after 3 ML

at 550 °C. The reported value of T_{cs} for GaSb is 480 °C.[11] If lattice mismatch were the dominant factor determining dot diameter, one would expect an increase in mismatch to result in a decrease of dot diameter, as observed for $In_xGa_{1-x}As/GaAs$.[13] Our results with InSb dots larger than GaSb dots suggest that other factors such as surface energy, T_{cs}, elastic coefficients, and growth temperature are important.

Compared to GaSb, AlSb has a comparable lattice mismatch with GaAs, 8.2%, and a larger T_{cs}, 520 °C.[11] No dots are formed after 3 ML of AlSb on GaAs at 500 °C, conditions which produced GaSb dots. Nanometer scale dots are present after 4 ML AlSb at 520 °C: density$\cong 6\times 10^{9}/cm^2$, height$=87\pm 23$ Å, and diameter $=560\pm 130$ Å. The dots are not as uniform as achieved for InAs, InSb, and GaSb. We note that AlSb is highly reactive in air. The resulting oxide may alter the apparent size and shape of the dots. As discussed later, Raman measurements indicate that an inner core of unoxidized material is present in the dots.[14]

Because of the change in anion, the growth of (In,Ga,Al)Sb dots on GaAs is more complicated than the InAs/GaAs system. STM imaging shows that the $c(4\times 4)$ GaAs reconstruction consists of a complete layer of Ga, followed by a complete layer of As and an additional 3/4 layer of As on top.[15] Hence, when depositing GaSb (AlSb) on GaAs, part of the first monolayer of Ga (Al) may form GaAs (AlAs) rather than GaSb (AlSb). This fact might explain why the wetting layer thickness appears to be larger for GaSb and AlSb than InAs, even though the lattice mismatches are comparable.

Work in the InGaAs/GaAs system showed that larger mismatches result in thinner wetting layers.[8,13] Hence, we might expect the InSb/GaAs system, with a 14% lattice mismatch, to have a smaller wetting layer thickness than GaSb or AlSb. Our value for the onset of InSb dot formation, 1.5 ML, is indeed smaller than the GaSb and AlSb values.. It is comparable to measurements of 1.5 ML[2] and 1.8 ML[1,5] for InAs on GaAs. In the case of InSb on $c(4\times 4)$ GaAs, some of the initial In could incorporate as InAs rather than InSb. Additional As–Sb exchange reactions may be possible, although Raman scattering measurements suggest that a GaAs layer is stable under an Sb flux to temperatures of 700 °C[11] and single monolayers of As in a GaSb layer are well defined at a growth temperature of 400 °C.[16] Raman measurements have also been performed on the nanometer-scale dots.[14] The energies of the vibrational modes of the dots indicate that only a small amount of Ga or As from the substrate has become incorporated in the GaSb and InSb dots. However, we observe a two-mode behavior from the ''AlSb'' dots, indicating that a substantial amount of Ga is incorporated into the dots formed during AlSb deposition.

Monte Carlo studies of epitaxial growth predict the onset of islanding in systems with sufficient mismatch.[17] Predictions based upon a simple kinetic model suggest that monodisperse nanoparticles may be grown on a surface if growth kinetics and island nucleation are property controlled.[18] To our knowledge, however, no theory exists which can predict the onset of 3D growth and dot size for InAs/GaAs or other SK growth systems. Studies of antimonide dots, combined with the existing data based on In(Ga,Al)As dots, should lead to a better understanding of the role of strain, surface energy, and growth conditions. A recent theory predicts the formation of platelets as a precursor to dot growth.[19] We have observed platelet formation after 1–2 ML InSb or GaSb on GaAs by *in situ* scanning tunneling microscopy.[20]

In summary, InSb, GaSb, and AlSb can grow on GaAs by the Stranski–Krastanov mode. After deposition of a planar wetting layer, lattice mismatch leads to the formation of islands. Under the appropriate MBE growth conditions, islands of InSb and GaSb are isolated and relatively uniform with nanometer-scale dimensions. Experiments are in progress to confirm quantum properties of these dots.

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