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Observation of change in critical thickness of In droplet formation on GaAs(100)

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Abstract

We present a study on the formation of In droplets on GaAs(100) substrates as functions of substrate temperature and monolayer (ML) deposition by using molecular beam epitaxy (MBE) and atomic force microscopy (AFM). We specifically reveal the change in critical thickness of In deposition to form In droplets at different substrate temperatures. At a relatively high substrate temperature, the critical thickness of In droplets becomes relatively thinner as the amount of As atoms on the surface decreases. The control of the size and density of In droplets is also systematically discussed. This study provides an aid in understanding the formation of In droplets and thus can find applications in the formation of quantum structures and/or nanostructures based on droplet epitaxy.

1. Introduction

Because of their potential application in optoelectronic devices such as lasers, detectors, and other novel quantum dot based devices, low-dimensional quantum dots (QDs) have attracted an increased attention [1–4]. As a result, $In_xGa_{1-x}As/GaAs$ quantum dots grown on GaAs(100) substrates using the Stranski–Krastanov (SK) growth mode [5] have been extensively investigated [6–12]. In SK mode based InAs QD growth, which is one of the most widely investigated QD fabrication methods, it is generally accepted that QDs are formed through a coherent surface deformation after deposition of at least 1.6 ML of InAs on GaAs(100) surface. This portion of material that is believed to induce the compressive strain by lattice mismatch is called the two-dimensional (2D) wetting layer. The amount of wetting layer, in fact, is less than the nominal thickness due to material transfer into QDs to compensate the reduction of strain in the film and the expansion of surface area [13]. With a 2D to 3D transition, the material in the film is sucked into the relaxed QDs, which more rigorously occurs around island sites, thus reducing the thickness of the wetting layer. The 2D to 3D transition, namely from the 2D wetting layer to low-dimensional QD formation, is typically observed by reflection high-energy electron diffraction (RHEED). In a RHEED study, QD formation is observed with its characteristic spotty pattern from the streaky pattern of the 2D wetting layer [14], and it is very sensitive to additional 0.01 ML deposition. 2D wetting layer formation is always accompanied in the SK based QD growth due to the nature of the growth mechanism, the lattice mismatch.

While low-dimensional quantum dots are well studied by using the SK growth mode, another growth approach was required for the formation of quantum structures and/or nanostructures in material systems without sufficient lattice mismatch. Such material systems as $Al_xGa_{1-x}As$/GaAs and GaAs/GaAs do not provide sufficient lattice mismatch to utilize the SK growth mode. Thus, droplet epitaxy was introduced [15], and it has been used to fabricate various quantum structures and nanostructures [16–22]. In III–V droplet epitaxy, atomic or molecular beams of metal atoms (Ga, In and Al) are introduced to a GaAs substrate without As atoms supplied. This forms metal droplets on the surface, such as Ga, In and Al droplets on GaAs substrates. The size and density of the droplets can be engineered by modifying the growth conditions such as substrate temperature and deposition amount [26]. In the next step, these metal particles can be crystallized into GaAs, InAs, and AlAs by exposing the droplets to subsequent As flux. This process is also denoted as ‘arsenization’ [17]. During this process, these metal droplets can be converted into various shapes of nanostructures, such as elongated islands with and without holes [19, 22], and single or double quantum ring structures [20], and the shape of the droplets can be kept, too [16]. These structures themselves are interesting to study. In addition, another advantage of these nanostructures is that they can be used as a template for further growth. Such an approach has been used to realize a unique ensemble of quantum dots [16, 19, 22]. Recently, the formation of high-quality InAs QDs by using droplet epitaxy has been demonstrated [23]. Based on the description of droplet epitaxy, one could imagine that there would be no wetting layer formation during the formation of In droplets. However, there is indeed still wetting layer formation before the formation of In droplets on the GaAs surface in droplet epitaxy.

In this study, we report on the observation of different critical thickness of In droplet formation on GaAs(100) surface by molecular beam epitaxy (MBE). The formation of In droplets with the variation of substrate temperatures and the amount of In atom deposition is systematically studied. The difference in critical thickness of droplet formation is kinetically and thermodynamically explained by the change in As atoms on the surface. The understanding of the formation of In droplets can play a significant role in the study of the formation of QDs and further the development of QD-based devices.

2. Experiments

In this work, samples were grown on epitaxy-ready 625 μm thick GaAs(100) substrates by molecular beam epitaxy (MBE). The growth procedures of samples were carefully monitored with a reflection high-energy electron diffraction (RHEED) system. Prior to introducing to a growth chamber, samples were degassed in a degassing chamber at 350 °C for half an hour. After the degassing of the substrates, surface oxide was desorbed from GaAs surface at 600 °C for defect-free GaAs buffer layer growth. A half micron of GaAs buffer layer was grown at 600 °C under a beam equivalent pressure (BEP) of 6.4 μTorr, highly over-pressured As flux. The nominal growth rate of GaAs was 0.7 monolayer (ML) per second, which was deduced by the *in situ* RHEED system. A 10 min annealing of the GaAs buffer layer took place to stabilize the surface directly after the buffer growth. A characteristic asymmetric (2×4) surface reconstruction was observed on this surface by the phosphorescent RHEED screen. Then, the substrate temperature was gradually decreased to 540 °C and the As valve was closed to discontinue the supply of As_4. From this point, the substrate temperature was decreased to

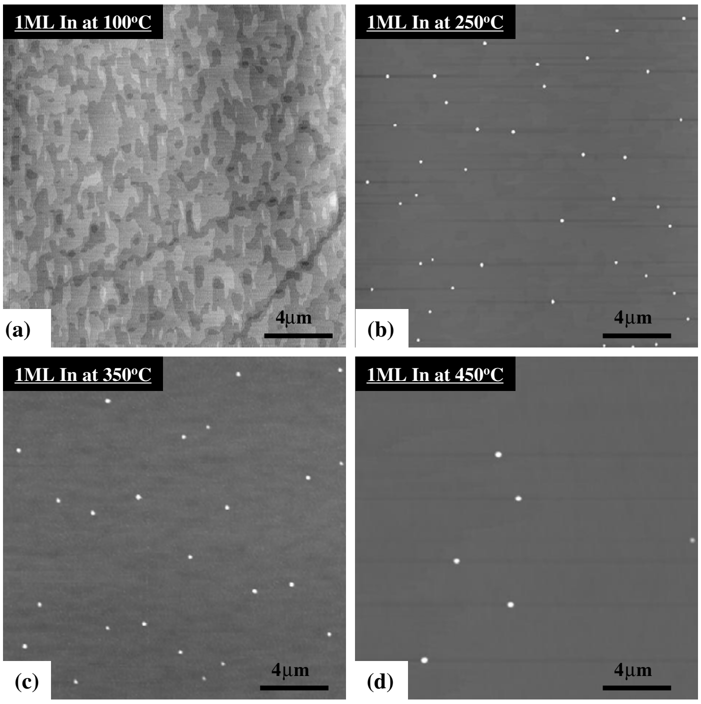

Figure 1. AFM images of substrate temperature variation at a fixed amount of In deposition. These figures show the density change with various substrate temperatures. Each figure shows 1 ML deposition (corresponding amount of InAs) at (a) 100 °C, at (b) 250 °C, at (c) 350 °C, and at (d) 450 °C. Figures are 20 × 20 μm.

each growth temperature: 100, 250, 350 and 450 °C. We systemically varied the amount of In deposition (from 0.5 to 5 ML) as a function of substrate temperature. The nominal growth rate of In was 0.08 ML s^{-1} for all samples. Here, the amount of In deposition in ML is an equivalent amount of InAs when sufficient As_4 is supplied. Typically, In was deposited at a background pressure below 2×10^{-9} Torr in the growth chamber to prevent the effect of background As pressure on the samples. The substrate temperature was quenched right after the termination of each growth and samples were transferred out of the chamber for the atomic force microscopy morphology measurement in air.

3. Results and discussions

To study the difference in monolayer (ML) coverage during the formation of In droplets, we start with the variation of substrate temperatures for a fixed amount of In deposition (1 ML). It is known that a few ML of deposition can form In droplets over almost all the growth window [23]: from room temperature to 500 °C. From this perspective, a relatively small amount (1 ML) was chosen to start with. In figure 1, the substrate temperature variation set of samples is shown with 1 ML deposition (an equivalent amount of InAs deposition when sufficient As_4 is supplied): at (a) 100 °C, (b) 250 °C, (c) 350 °C, and (d) 450 °C. First, a noticeable difference in samples of this set is that In droplets were formed at 250, 350, and 450 °C while droplet formation was not observed at 100 °C. This can be explained by the interaction of applied In atoms with existing As atoms on the surface due to surface

Table 1. Average In droplet density cm^{-2} at various substrate temperatures with varied amount of deposition. The height and diameter of the In droplets are given accordingly.

Growth Temp (°C)	Figure No.	In deposition (ML)	Droplet density (cm^2)	Droplet height (nm)	Droplet diameter (nm)
250	1(b)	1	4.17×10^7	40	250
350	1(c)	1	2.65×10^7	55	400
450	1(d)	1	1.57×10^6	110	500
100	2(b)	2	2.2×10^8	35	150
100	2(c)	5	1.5×10^8	75	230
350	4(b)	0.5	8.4×10^5	55	350

reconstructions. Although there is still a controversy about whether the amount of As atoms can be different depending on surface reconstructions, it is known that there is presumably ∼1.75 ML of As atoms present on the surface at around 100 °C [24]. There is an inverse relationship between the amount of surface As atoms and substrate temperature: that is, the amount of As atoms on the surface decreases with increasing substrate temperature. Therefore, the applied In atoms (1 ML) formed a 2D layer of InAs at 100 °C (see figure 1(a)). At 250 °C the same amount of In deposition (1 ML) resulted in the formation of In droplets (see figure 1(b)). The density and size of droplets are provided in table 1. The density of the droplet was 4.17×10^7 cm^{-2} and the average droplet size was 40 nm in height and 250 nm in diameter. The formation of In droplets at an elevated substrate temperature (250 °C) even when the amount of deposition is same (1 ML) can be due to the presence of a lower amount of As atoms on the surface at an increased substrate temperature: the inverse relationship between substrate temperature and surface As atoms. From this observation, therefore, we can always expect the formation of In droplets with 1 ML deposition at an increased temperature (above 250 °C), and our results confirm this speculation. As the substrate temperature was increased to 350 °C (see figure 1(c)), the formation of In droplets was observed with 1 ML deposition, confirming our speculation. Due to the higher length of adatom diffusion (surface atom), the density is noticeably decreased to 2.65×10^7 cm^{-2} and thus the average size of droplets became relatively larger: 55 nm in height and 400 nm in diameter. The ratio of density of samples (350/250 °C) was 0.63 and the size ratio was 1.4 in height and 1.6 in diameter, which appears a fair tradeoff between size and density of droplets. The decrease in density of droplets with the increased substrate temperature was a similar result as in our previous study on Ga droplets [25]. We now can expect two things when we further increase the substrate temperature with 1 ML deposition: (1) the formation of In droplets and (2) the reduction in density and the increase in size of droplets. To confirm our speculation, 1 ML deposition at 450 °C was performed, and the result is shown in figure 1(d). With the increase of substrate temperature to 450 °C, the density was further significantly decreased to 1.57×10^6 cm^{-2}, which is about an order of magnitude decrease from the sample grown at the substrate temperature of 350 °C. As a result, the average size of droplets was increased to 110 nm in height and 500 nm in diameter. While the increase in height of droplets was by 200%, the diameter of the droplets was increased by only 20% as compared to the sample grown at 350 °C. This set clearly demonstrates the change in critical thickness to form In droplets on GaAs(100) surface at different substrate temperature (from 100 to 450 °C) with a fixed ML deposition (1 ML). The critical thickness of droplet is mainly affected by the change in the amount of As atoms on the surface at various substrate temperatures. Also, the response in size and density of In droplets to various substrate temperatures is clearly described.

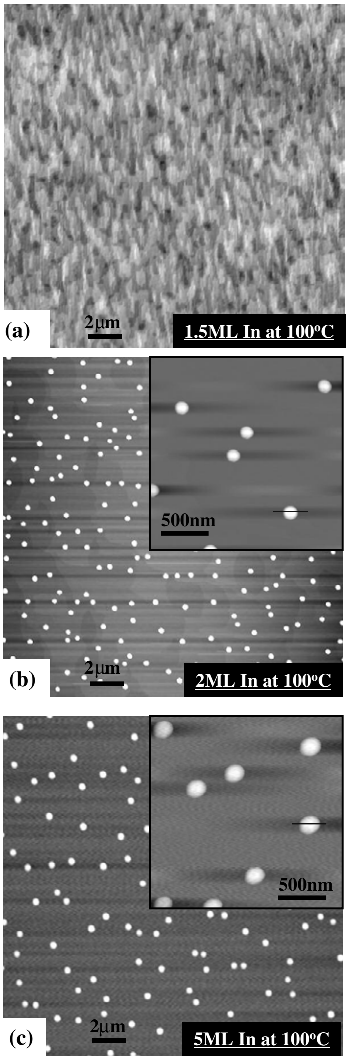

Figure 2. AFM results of In monolayer coverage variation at a fixed substrate temperature: (a) 1.5 ML, (b) 2.0 ML, and (c) 5.0 ML of In deposition at 100 °C (corresponding amount of InAs). Larger figures are 20 × 20 μm and smaller (enlarged) figures are 2 × 2 μm. Black lines in figures 1(b) and (c) (2 × 2 μm) are line profiles shown in figures (a) and (b).

From the experiment above, we can now always expect the formation of In droplets at above 250 °C with 1 ML coverage; however, we are not certain of the critical thickness of In droplet formation at 100 °C. To further investigate the critical thickness, we now vary the ML deposition at a fixed substrate temperature (at 100 °C). Figure 2 shows the ML variation set at a fixed growth temperature of 100 °C. With the further increase of In deposition (from the set above) to 1.5 ML, we still did not observe the formation of In droplets in figure 2(a). This makes a good sense if the amount of existing As atoms on this surface at 100 °C is ~1.75 ML and thus all of the deposited material formed a 2D InAs layer rather than forming In droplets. As seen in figure 2(a), the surface is smooth with ML steps. There are several different heights of steps with different colour scales. Darker regions are lower steps in height and vice versa.

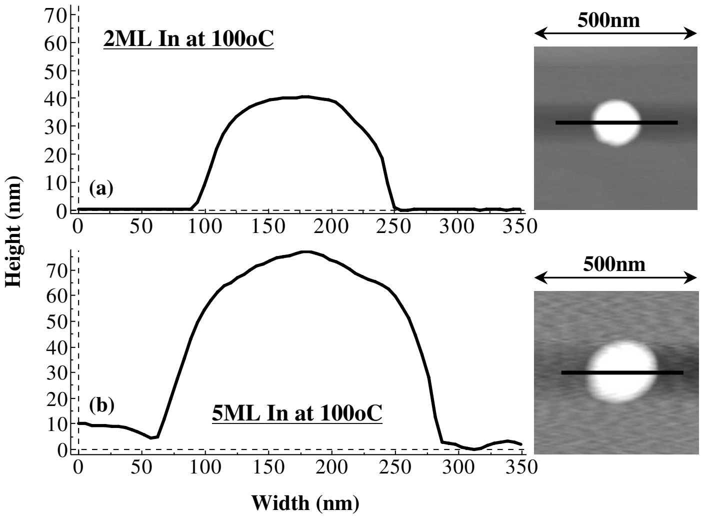

Figure 3. Corresponding line profiles indicated as black lines in figures 1(b) and (c) (2 × 2 μm AFM images). These figures explain the increased volume of In droplets with increased amount of deposition. Each line profile corresponds to each figure; i.e. 1(b)–2(a) and 1(c)–2(b). Each figure shows the individual line-profiled structures as well as the amount of deposition in the monolayer with substrate temperature.

The difference in height of the adjacent step was ~3 Å, which is known to be the step height of InAs. With increased ML coverage to 2 ML, In droplets appeared (see figure 2(b)). The droplets were typically 35 nm in height and 150 nm in diameter, as shown in table 1. This average size of droplets is relatively smaller than that of samples grown at higher temperatures such as 250 and 350 °C. This can be due to the decrease in diffusion length of the adatom, induced by the decrease in substrate temperature. As a result, the density of In droplets was relatively high, 2.2×10^8 cm^2, which is one order of magnitude higher than that of samples grown at 250 and 350 °C. The formation of droplets with 2 ML deposition at 100 °C matches well with the previous observation of the presence of ~1.75 ML of surface As atoms at 100 °C, and thus logically can be explained [24]. The excess atoms after interacting with As atoms resulted in the formation of In droplets through the Volmer–Webber growth mode [26]. In this growth mode, the equilibrium status of these metal atoms on the surface is in the form of droplets rather than spreading over the surface (2D layer). Figure 2(c) shows the resulting surface with 5 ML of In deposition at the substrate temperature of 100 °C. While the density was about the same as that of the sample grown with 2 ML deposition, the size of droplets was increased to 75 nm in height and 230 nm in diameter on average. The size of In droplets with increased ML deposition is more clearly seen in the insets in figures 2(b) and (c), and in the line-profiles across the droplets in figures 3(a) and (b). This significant increase in size of In droplets (from 35 to 75 nm) with increased ML deposition (from 2 to 5 ML) is a similar result to the observation above on the increase in size of In droplets with increased substrate temperature (from 350 to 450 °C) for a fixed deposition of 1 ML (see figure 1). For 1 ML deposition, the increase in height of In droplets was more obvious with the variation of the substrate temperatures from 350 and 450 °C (see figure 1 and table 1). However, the increase in diameter of In droplets was more obvious than the increase in height when the substrate temperature was varied from 250 and 350 °C. From this observation, we might speculate that the increase in droplet size is favourable for the lateral direction (increase in diameter) with In adatom incorporation into

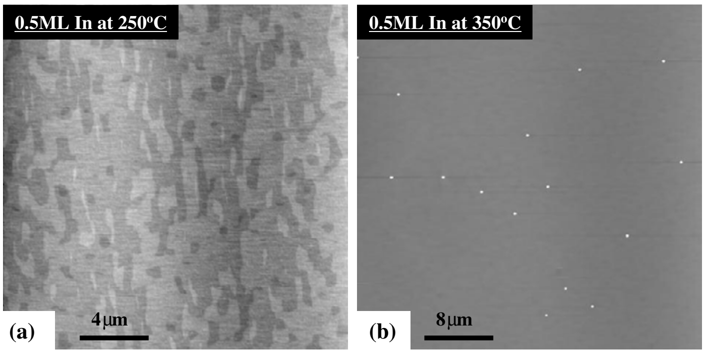

Figure 4. Resulting surfaces by AFM after depositing the same amount of In (0.5 ML) at two different substrate temperatures: (a) 0.5 ML deposition (corresponding amount of InAs) at 250 °C, and (b) 0.5 ML deposition at 350 °C. These figures show that the critical thickness of In droplets is different for different substrate temperatures. (a) is 20 × 20 μm and (b) is 40 × 40 μm.

already formed In droplets at the beginning stage. Then, the expansion of size is not favourable for growth only along the lateral direction, thus the droplet expands in the vertical direction, which results in an increase in height. Whether this small number of observations is correct, the shape transition is certain to reduce the surface area, thus causing the surface energy to be in equilibrium. From our previous study on Ga droplets [26], the size of Ga droplets was strongly dependent on both the substrate temperature and the amount of deposition, while the density was mainly determined only by the substrate temperature. It appears that In droplets show a similar behavior in terms of size and density response to substrate temperature and ML deposition variations. There is observed a slight decrease in density of In droplets from the 2 ML deposition in figure 2(b) to the 5 ML deposition in figure 2(c). This decrease in density of droplets can be explained by Oswald ripening [27]. With the 5 ML deposition, the time taken for the growth lasted longer by 37 s than the 2 ML deposition based on the nominal growth rate of 0.08 ML s^{-1}. This set, the variation of ML deposition at a fixed substrate temperature, clearly demonstrated that the critical thickness of In droplets at the substrate temperature of 100 °C is between 1.5 and 2.0 ML, most probably ~1.75 ML, and also the size increase with increased ML deposition was explained.

Figure 4 shows sub-ML deposition at two different substrate temperatures: 250 and 350 °C. While the formation of In droplets was observed at 350 °C with 0.5 ML (see figure 4(b)), In droplets did not form with the same amount of deposition at 250 °C (see figure 4(a)). This is another indication of the decrease in the amount of As atoms with increased substrate temperature: the inverse relationship. Droplets were 55 nm in height and 350 nm in diameter with very low density of 8.4×10^5 cm^2 in figure 4(b). As discussed for figure 2, the density of droplets is not much affected by the amount of In deposition at the same substrate temperature. However, here the density of In droplets was significantly different between samples in figures 1(c) and 4(b) in spite of the fact that both samples were grown at the same substrate temperature of 350 °C. We have grown more samples with ML coverage variation at 350 and 450 °C, although the results are not presented in this paper. In droplets did not form with further reduced deposition of 0.3 ML at 350 °C, and also, the result was very similar to the set in figure 2 in that the density did not much change above 1 ML. From these observations, we can conclude that the critical thickness of In droplets on GaAs(100) surface at 350 °C is ~0.5 ML. We can speculate that the difference in density of In droplets between samples in figures 1(c) and 4(b) can be explained by the onset of nucleation of In droplets at 350 °C with a half ML deposition. The formation of In droplets with 1 ML deposition at 250 °C in figure 1(b) and the resulting surface with 0.5 ML at the same substrate temperature in figure 4(a) indicate that the critical thickness of In droplets at 250 °C is between 0.5 and 1.0 ML, likely close to 1.0 ML. Based on the observations we have discussed so far, we can speculate that the critical thickness of In droplets at 450 °C can be either similar to that at 350 °C or a slightly lower deposition. These two samples shown in figure 4 clearly provide more understanding of the critical thickness of In droplets.

4. Conclusion

In summary, to study the change in critical thickness and the behaviour of In droplets, the variation of substrate temperature and ML deposition were investigated on GaAs(100) substrates by molecular beam epitaxy (MBE). The critical thickness of In droplets was observed to be an inverse relationship between substrate temperature and amount of As atoms on surface. Specifically, the critical thickness of In droplets is between 1.5 and 2.0 ML at the substrate temperature of 100 °C and between 0.5 and 1.0 ML at 250 °C and around 0.5 ML at 350 °C. This observation suggests that the critical thickness of In droplets at 450 °C can be 0.5 ML or a little less. The size of In droplets was dependent on both the substrate temperature and ML deposition. The density of droplets was mainly dependent on the substrate temperature. This study can find applications in optoelectronics and help in understanding the formation of InAs quantum dots without forming a strained two dimensional wetting layer and/or under inefficient substrate lattice mismatches.

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