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Surface Science 601 (2007) 2438–2444
SURFACE SCIENCE
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Shape cycle of Ga clusters on GaAs during coalescence growth

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Received 15 July 2006; accepted for publication 3 April 2007
Available online 11 April 2007

Abstract

GaAs(1 0 0) was heated above its decomposition temperature of 585 °C bringing it into a phase separation regime where the thermodynamic favoured state is liquid Ga clusters on the surface. Varying the annealing times and temperatures provided an overview of the clustering at all stages from transitioning ripening at lower temperatures to coalescence at higher temperatures. We observed a shape cycle between round and rectangular shaped clusters during the growth. This cycle is driven by subcluster etching where pits are formed under clusters during the growth due to preferential loss of As through the liquid Ga cluster. The newly observed shape cycle is compared to a shape cycle observed previously in In on InP illustrating that shape cycles are a common feature of the decomposition of Group III–V semiconductors.

Keywords: Surface thermodynamics (including phase transitions); Surface structure, morphology, roughness, and topography; Gallium arsenide; Clusters; Semiconducting surfaces

1. Introduction

Thin films on gallium arsenide (GaAs) have unique applications for opto-electronic integration and high frequency devices and therefore is an important system to study. For such devices, high degrees of flatness are required which necessitate a large degree of control of the growth parameters. GaAs is also fundamentally interesting as subcluster etching, i.e., the formation of depressions under clusters, has been observed after the growth of gallium (Ga) clusters [1]. With the increasing importance of materials created on the nanoscale, there comes fundamental interest in self assembled structures and the limits of inherent order in the cluster size and spatial distributions as well as cluster shape. Prior studies show shape cycles in Ag on Si(0 0 1) [2], Ge on Si(0 0 1) [3], and most relevant to the current work In on InP(0 0 1) [4].

Clustering of Ga on GaAs is observed when GaAs is heated above temperatures of about 585 °C. This is the decomposition temperature at which the lattice structure begins to break down and there is a preferential loss of arsenic (As) from the surface. This results in an excess of liquid Ga and once a sufficiently high surface concentration of Ga is reached, cluster nucleation begins and phase separation occurs. The Ga on GaAs(1 0 0) growth mechanism is initially through ripening and then through static coalescence [5]. As the late stage clustering proceeds there are three processes: (i) As diffuses through the substrate lattice and evaporates from the surface, (ii) surface Ga diffuses into clusters and the exposed As desorbs from the surface, and (iii) As diffuses through the liquid Ga cluster and evaporates. The thermodynamic data for Ga on GaAs(1 0 0) are well known and an examination of the diffusion coefficients shows a faster loss of As through a liquid Ga cluster than from the substrate or the surface [1]. The result is subcluster etching where the cluster etches into the surface during growth.

In this paper, we observe the effect of this subcluster etching which is to drive a shape cycle from round to rectangular based and back to round clusters.

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0039-6028/$ - see front matter
doi:10.1016/j.susc.2007.04.019

2. Experimental

Samples of approximate size 1 cm by 1 cm were cut from a polished GaAs(1 0 0) wafer and heated in the heating stage of a Group III–V molecular beam epitaxy (MBE) chamber. The chamber is maintained with a base pressure less than 10^{-8} Pa. The sample was heated by indirect electron bombardment from a high current filament. The samples were heated above the decomposition temperatures with a range of about 585–750 °C with annealing times of 3–8 min. The temperature was measured with a thermocouple placed near the sample surface. The experiments done are listed in Table 1 with sample number, stage of growth, and annealing time. The pre-coalescence stage was annealed with temperatures under 600 °C, the coalescence stage is observed for temperatures in the range of 600–680 °C, and temperatures above 680 °C result in such a high fraction of liquid Ga on the surface that a large scale flowing aggregation forms.

Samples are classified by a newly introduced parameter ψ, which represents the fraction (in %) of the surface covered by Ga. This parameter is necessary as the traditional sample characterization by temperature and annealing time is not suitable for the current study and in situ analysis was unavailable. The temperature/time window for coalescence growth is rather narrow, with suitable temperatures ranging from 600 °C to less than 700 °C and annealing times from at least 3 min to about 15 min at the higher temperatures. The narrow window for these parameters is generally due to the non-equilibrium behaviour of the system. More specifically, the temperature must sufficiently exceed the decomposition threshold at 585 °C, but must allow the coalescence process to evolve without crossing into the onset of flow-processes or cohesive aggregation, which occur at areal coverages near 100%. Annealing temperatures must exceed the pre-coalescence range but must again be kept short enough to not reach too high areal coverages. With both temperature and annealing time to be very sensitive parameters, the respective error sources in their experimental measurement become critical. In the case of the temperature, calibration errors of the thermocouple and systematic errors of thermocouple/sample/sample holder thermal contact must be taken into account. Replacing the thermocouple with a pyrometer does not significantly improve this situation as calibration steps are again required. In addition, a wavelength of the pyrometer has to be chosen for which GaAs is not transparent, which infringes on the precise measurements of temperatures in the lower range. For the annealing time, again systematic errors due to heating and particularly cooling rate variations with the thermal contact to the sample holder become important. Most critically though, the fact that both temperature and annealing time are parameters needed to specify the extent of coalescence growth prohibits their independent use. Temperature variations enter the progression of the process through a Boltzmann term because the chemical decomposition of GaAs is an activated process; the annealing time is a linear parameter for the progression of the process. Thus, characterizing the system requires two independent parameter measurements, each with statistical and systematic errors. Their combination would further require an error propagation discussion.

Instead, the samples are characterized by a single parameter measurable after sample preparation. Temperature and annealing times in this approach are only used as an estimate of the stage and progression of the final morphology; the actual result is characterized by ψ. We have chosen this parameter as follows: To be a useful parameter, ψ must reflect in a steady, continuous fashion both the time and temperature dependent progression of the sample. In turn, neither of these dependencies must be linear, relieving us of the need for a quantitative formula for the cluster growth rate (which has not yet been developed for coalescence growth). Thus, we chose ψ to be the Ga coverage; this parameter does not only fulfil the requirements as stated above, but also allows us very directly to separate late stage coalescence growth from flow-dominated features and cohesive aggregation which occur close to 100% coverage. Table 1 is a list of all samples prepared with the stage of growth and value of ψ. Fig. 1 is a phase diagram indicating the stage of cluster formation as a function of ψ.

Table 1
List of samples with stage of growth and annealing times

Sample number	Stage	ψ (%)
G1	Pre-coalescence	1.53
G2	Pre-coalescence	1.65
G3	Pre-coalescence	2.10
G4	Pre-coalescence	5.00
G5	Pre-coalescence	7.89
G6	Pre-coalescence	12.7
G7	Early coalescence	20.8
G8	Early coalescence	25.5
G9	Early coalescence	25.8
G10	Early coalescence	37.1
G11	Coalescence	41.0
G12	Coalescence	43.3
G13	Coalescence	43.3
G14	Coalescence	50.2
G15	Coalescence	51.7
G16	Coalescence	56.6
G17	Cohesive aggregation	75.3

Scanning electron microscopy (SEM) was done on all samples to obtain surface images and the data analysis was done using these images. The SEM images were produced using an Hitachi S-4500 field emission SEM with EDX system at Surface Science Western of the University of Western Ontario. The primary electron beam had energy of 10 KeV and resolutions of $\leqslant$5 nm were obtained. EDX (energy dispersive X-ray) was used to confirm the clusters on the surface were Ga and the surrounding surface was GaAs.

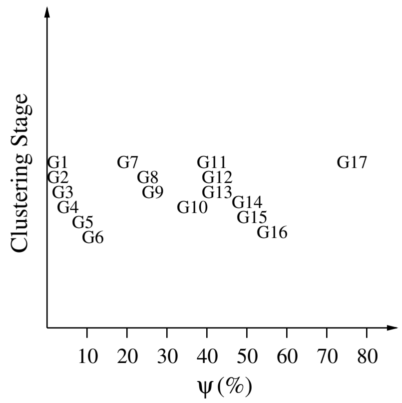

Fig. 1. Phase diagram of clustering stage vs surface coverage. Solid circles represent samples G1–G6 and are in a pre-coalescence phase, open circles represent samples G7–G10 and are in early coalescence phase, solid squares represent samples G11–G15 and are in the coalescence phase, and open circles represent samples G16 and G17 and are in the cohesive aggregation phase.

3. Results

This section contains images which show, for the first time, the existence of shape cycles in Ga on GaAs. The images demonstrate that the clustering process includes a transition from round to rectangular clusters in growth where clusters are still comparatively small. The clusters then go back to a round shape at intermediate sizes and finally the last stage of cluster formation shows a coexistence of round clusters with rectangular ones.

The early shape cycle is shown in Figs. 2–5 where clusters are initially small and round as seen in Fig. 2 (sample G2). In this sample, the areal coverage of Gas is $\psi = 1.65\%$. All clusters have round bases where the cluster contacts the surface. This clustering is a typical pattern of those observed in other liquid film systems such as Sn/Si [6,7]. The next two images, Figs. 3 and 4, show the rectangular phase of the early stage shape cycle. These figures

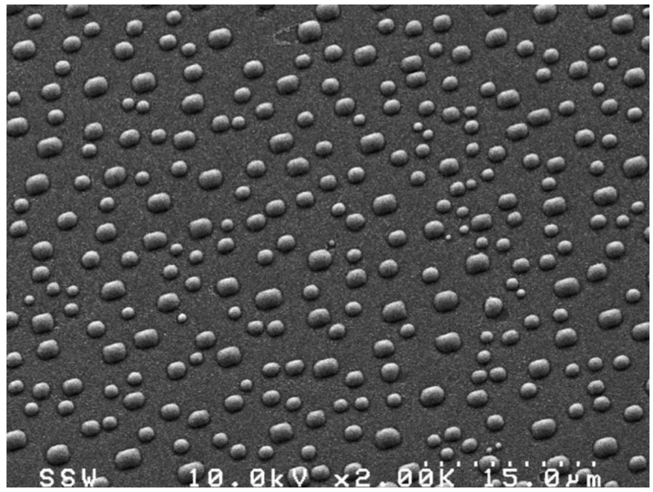

Fig. 3. SEM of Ga on GaAs(100) in pre-coalescence stage growth. Sample G7, annealing time = 7 min.

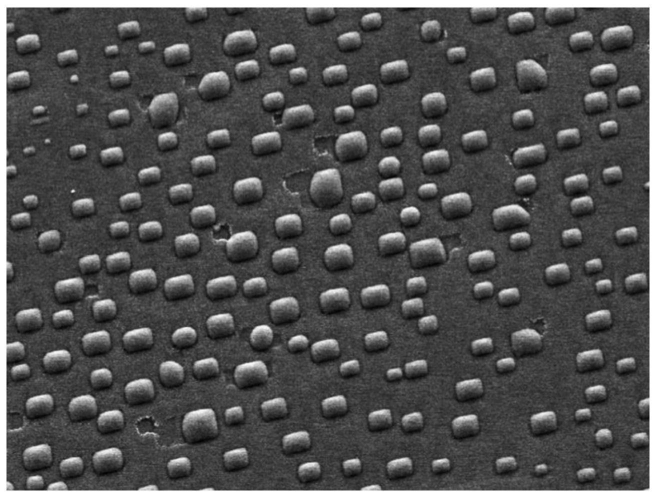

Fig. 4. SEM of Ga on GaAs(100) in pre-coalescence stage growth. Sample G8, annealing time = 7 min.

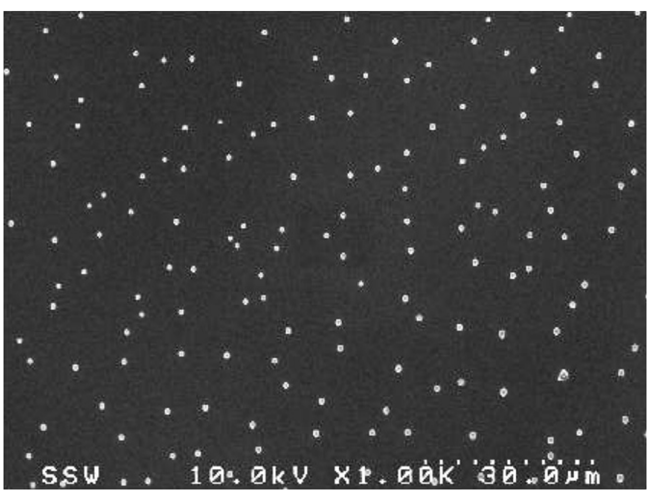

Fig. 2. SEM of Ga on GaAs in pre-coalescence stage growth. Sample G2, annealing time = 5 min.

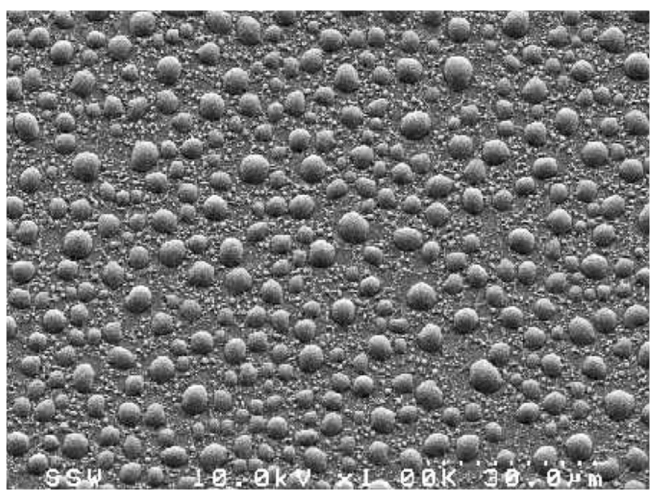

Fig. 5. SEM of Ga on GaAs in early coalescence stage growth. Sample G12, annealing time = 3 min.

have clusters have areal coverages of $\psi = 20.8\%$ and $\psi = 25.5\%$ for runs G7 and G8, respectively, indicating that the clustering process is further along than in the sample shown in Fig. 2. In both figures, clusters have a rectangular interface but rounded clusters are stretched over the rectangular base. That this is the case is particularly evident in Fig. 4. In this figure, there are several places where two clusters have touched, merged, and the cluster has retracted exposing a rectangular shaped pit under the retracting cluster.

We discuss quantitatively below why the rectangular shaped pit is responsible for the shape of the cluster as the liquid cluster clings to the edge of the pit resulting in a rounded cluster with a rectangular base. We also emphasize that samples shown in Figs. 2–4 stretch the entire early stage phase of phase separation in the Ga/GaAs system. This is evident from the ψ values when compared with the surface phase diagram, Fig. 1 and is morphologically evident from the onset of cluster merges in Fig. 4. The sample in this figure can be seen as in transition to the late stage, but the late stage has not been reached as clusters merging does not yet dominate the cluster size distribution for this sample.

In the late stage, repetitive shape cycles are shown in Figs. 5–8. These figures show that as the clustering proceeds, the rectangular features of the clusters diminish so that while some rectangular nature is present, most clusters at any given time take on a more rounded shape. This is shown in Fig. 5 where there are larger clusters and the surface has an areal coverage of $\psi = 43.3\%$ indicating that the cluster growth is now in late stage and growth is via coalescence. This figure shows that while some clusters have partially straight edges, all clusters have rounded corners. The small clusters present are either round or rectangular or a combination of both as are freshly exposed subcluster depressions. This figure shows a transition in the shape cycle where clusters go from rectangular to round.

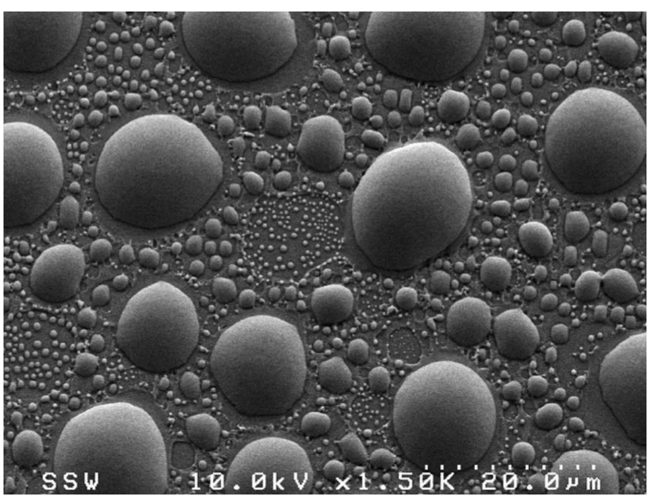

Fig. 6. SEM of Ga on GaAs in coalescence stage growth. Sample G15, annealing time = 5 min.

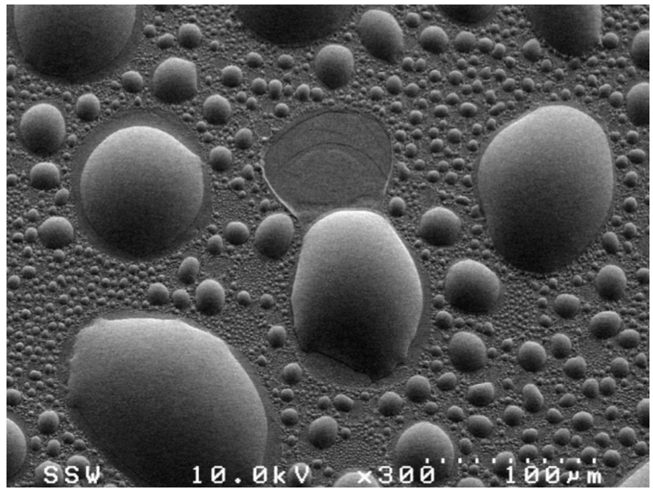

Fig. 7. SEM of Ga on GaAs in cohesive aggregation stage growth. Sample G16, annealing time = 5 min.

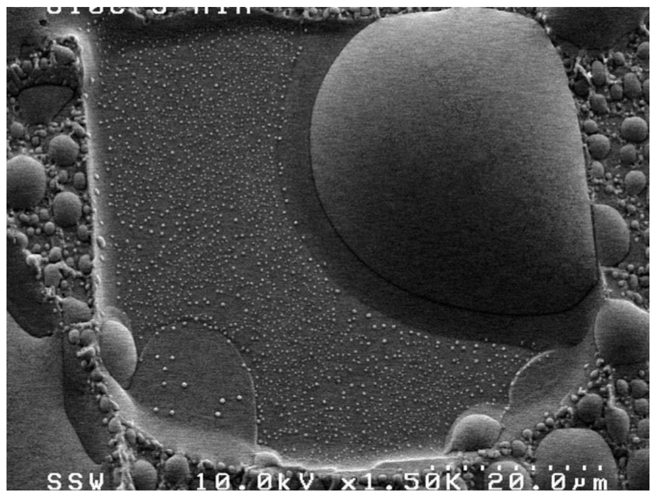

Fig. 8. SEM of Ga on GaAs in cohesive aggregation stage growth. Sample G16, annealing time = 5 min.

The next figure, Fig. 6 is later in the clustering process with $\psi =$ 51.7% and the majority of all clusters are rounded or elliptical as are the pits exposed after a coalescence event. This figure shows that the shape cycle repeats in recently clearly depressions. In the depressions, some of the larger secondary clusters have rectangular features while smaller secondary clusters are round. Some of the smaller recently exposed pits are also rectangular indicating the new beginning of the early shape cycle in clusters which have not yet begun to grow via coalescence.

The final three figures, Figs. 7–9 are from the same sample, G16, which has cluster growth via coalescence with an areal coverage of $\psi = 56.6\%$. The scale of each image is shown in the lower right hand corners. Fig. 7 shows clusters which are all round or elliptical with very few exceptions where clusters have a rectangular edge. The next two figures, Figs. 8 and 9 show examples of the final stage of the shape cycle where rectangular depressions are

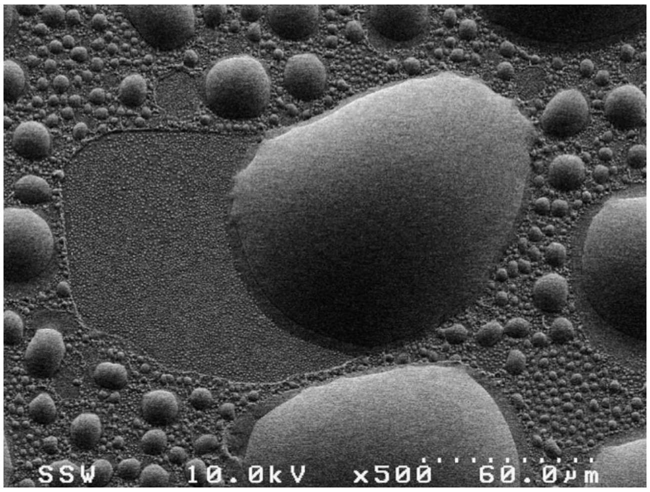

Fig. 9. SEM of Ga on GaAs in cohesive aggregation stage growth. Sample G16, annealing time = 5 min.

exposed after a cluster detached from the edges. These cluster would have had the same rectangular base as the clusters in the early stages of the shape cycle. Fig. 8 is an image of a cluster which was initially attached to the edges of the rectangular pit which detached once the energy of maintaining the rectangular base became too large. After detaching, the cluster retracted to one corner of the rectangular depression forming a partial spherical shape with two straight edges. Fig. 9 shows the shape cycle in a different way: This image shows a coalescence event where two large clusters touched and the retracting cluster revealed a rectangular subcluster depression.

4. Discussion

The shape cycle is a result of the subcluster etching which occurs after clusters form on the substrate. Initial clusters form once enough material is gathered. Clusters are initially spherically capped in shape as this is the most energetically favourable shape. Arsenic loss then continues faster through the cluster than from the surface so that initial subcluster depressions are round. As etching continues, rectangular pits form as certain low Miller index planes have slower etching rates than high index planes. The bottom plane is a 1 0 0 direction (parallel to surface) and has a very low etching rate. A favourably low interfacial energy causes the cluster to cling to the edges of the rectangular pit, stretching out the bottom of the cluster and causing a change from the spherically capped shape. Because the cluster has deviated from the spherical shape, it no longer has minimum surface to volume ratio. Eventually the rectangular shape is energetically unfavourable at which point the cluster will detach and form a partial sphere, typically in the corner of the pit. Subcluster etching begins under the reshaped cluster and the shape cycle repeats.

Information about the surface energies of the system may be determined by consideration of the surface energies of the two cluster shapes. At the point where the stretched, rectangular based cluster detaches from the edge of the depression to form a spherical cap shaped cluster, the energies of the two clusters must be equal, i.e.,

$$E_r - E_s = 0 \tag{1}$$

where E_r is the energy of the rectangular based cluster and E_s is the energy of the spherical cap cluster. The two different shaped clusters will have identical volume at the point of detachment therefore, we may equate the surface energies of the clusters. The energy of the spherical cap cluster, with radius r of the contact circle and height h is

$$E_s = \gamma_{sv}(A - \pi r^2) + \gamma_{cs}\pi r^2 + \gamma_{cv}(2\pi Rh) \tag{2}$$

where A is the area of the substrate, γ_{sv} is the surface tension between the surface and vacuum, γ_{cs} is the surface tension between the cluster and the substrate, γ_{cv} is the surface tension between the cluster and the vacuum. The surface energy of the rectangular based cluster in a depression of depth d is

$$E_r = \gamma_{sv}(A - ab) + \gamma_{cs}(ab + 2ad + 2bd) + \gamma_{cv}S \tag{3}$$

where S is the surface area, and a and b are the dimensions of the rectangle. The surface area of the rectangular based cluster may be determined, either by measurement or numerical methods [8]. We may also use the Young–Dupré equation

$$\gamma_{sv} = \gamma_{cs} + \gamma_{cv}\cos\theta \tag{4}$$

to provide another constraint on the surface tension on a system with angle θ between the cluster and the surface. Combining these equations with a known surface tension between the cluster and vacuum [9] provides a method of determining the unknown surface tensions between the cluster and surface and the surface and vacuum.

We note that these shape cycles are observed only in a narrow temperature interval for Ga/GaAs. This indicates that a full cycle requires a certain ratio of subcluster etching rates and cluster growth rates. When clusters grow too fast, etching is subdued and late stage coalescence growth occurs unaffected by etching-related processes. If clusters grow too slowly, etching would dominate, but even without etching, a proper late stage coalescence growth may be reached only after a period too long for the technical limitations of the experimental study. Concurrent but dominating etching would further disable the occurrence of a late stage coalescence growth as clusters would not reach a sufficient areal coverage to touch and merge frequently. Based on our experimental observations, we note that the etching and growth length scales in the Ga/GaAs system are such that full cluster shape cycles are confined to a narrow parameter window sensitively depending on both time and temperature. The experiments show clusters in the samples with values of $\psi = 20.8$, 25.5, and 25.8% have rectangular based shapes. The aspect ratio of clusters in these samples were measured and found to have a constant value of 1.32 ± 0.13 [8]. Samples with values of $\psi \leqslant 12.7\%$ have round clusters and samples with $\psi \geqslant 37.1\%$ have primarily round clusters with some associated rectangular features. As ψ has a dependence on both temperature and time, it cannot be used as a sole parameter to determine the percentage of clusters with rectangular features.

With the observation of the cycle in Ga/GaAs we can now connect this shape cycle with observations made in the In/InP system in which a late stage shape cycle was observed as clusters repeatedly transitioned between round and rectangular. This connection allows us to demonstrate that shape cycles are common at least to Group III–V semiconductor systems which show cluster growth via coalescence during the loss of the Group V element. In on InP(001) was studied experimentally in our group [4] and the results pertinent to our case are highlighted below. The system studied was In on InP(001) at 500 ± 15 °C and at this temperature, the cluster growth is via coalescence. Cluster formation and growth proceed via the same mechanism as outlined above: Above the decomposition temperature there is a continuous loss of P resulting in a supersaturation of In at the surface. The system then enters the phase separating regime where clusters grow through coalescence. Fig. 10 is an SEM micrograph of an In on InP surface after annealing at 500 °C for 10 min. Present in this figure are both large and small clusters and the measured cluster size distribution [4] indicates the bimodal nature of the cluster size distribution predicted by the theory [10] and indicate that the cluster size distribution follows a self similar growth like that observed in Ga on GaAs [7]. Also observed in this system was a distinct deviation from rounded cluster shapes and this is seen in Fig. 10 where a minority of the clusters have a rectangular nature either having a rectangular shape or one or more rectangular edges in the contact between the surface and cluster.

The clusters with rectangular features were observed to contribute an estimated 10% of the clusters present on the surface. By consideration of the cluster size relative to annealing time, it was seen that cluster size increases monotonically with time. This increase of cluster size with time, together with observations of multiple rectangular pits associated with a single round cluster as seen in the centre panel of Fig. 10 indicates that there is an oscillating shape cycle between round and rectangular based clusters in In on InP(001) which occurs during the sample annealing period.

A quantitative analysis of the cluster shape cycle was also provided with consideration of the etching rates as the subcluster depressions form during cluster growth. Depressions under clusters occur commonly in Group III–V compound semiconductors and this is illustrated in Fig. 11. In the top panel of this figure, it is seen that the subcluster depression is shallow compared to both the other dimensions of the depression and the cluster itself. The bottom panel, showing the surface after the Indium clusters have been chemically removed, indicates the coexistence of round and rectangular depressions. Further seen in this image from the contrast at the edges, is that the rectangular depressions appear deeper than the round ones.

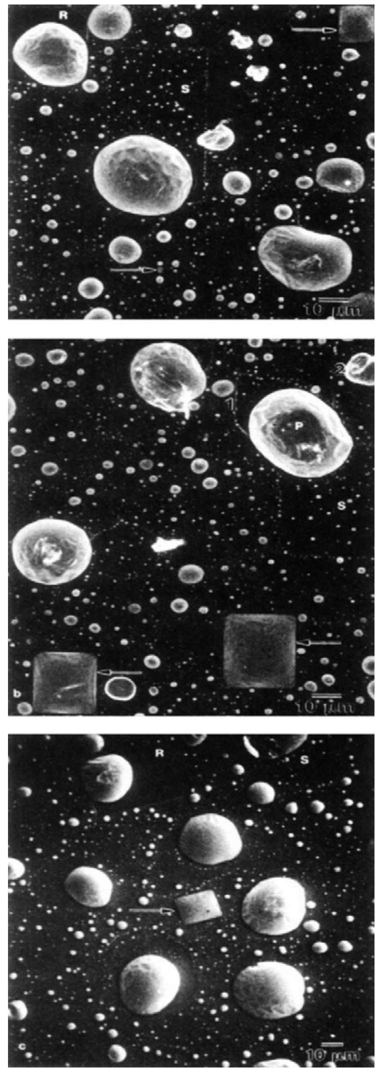

Fig. 10. SEM of In on InP(001) after annealing at 500 °C for 10 min [4]. The three images show two features of the cyclic shape changes. The first feature is that approximately 90% of the clusters are partially spherical with diameters of up to 10 μm. The second feature is that approximately 10% of clusters are associated with rectangular features either in the cluster itself as indicated by the arrows or in the underlying depression as indicated with the **R**.

Round depressions have been observed in other III–V compound semiconductors and the origin of the depressions in the Ga on GaAs has been discussed [1]. The same reasoning applies to depressions in In on InP and clustering phenomena on other decomposing III–V compound semiconductors. As the annealing proceeds there is a competition between the loss of the Group V element (P or As) via two processes (i) through bulk diffusion through the semiconductor and subsequent desorption from the surface and (ii) dissolution of the compound semiconductor into the growing group III cluster, followed by diffusion of the group V element to the cluster surface and desorption from that surface. Consideration of the thermodynamic data available for InP shows that the P loss is faster from areas beneath clusters [4].

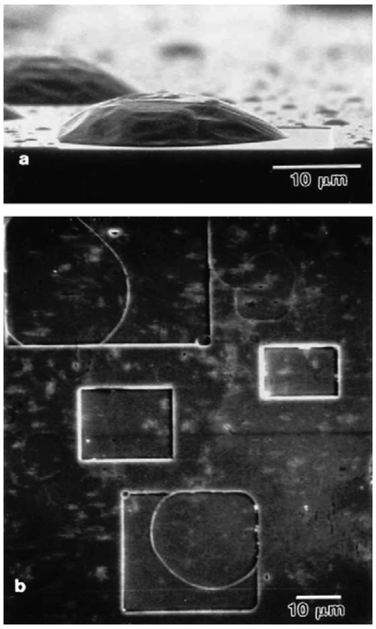

Fig. 11. SEM of In on InP(001) after annealing at 500 °C for 10 min [4]. (a) is a cross sectional image of an In cluster in a subcluster depression. The image shows that the depression has rectangular features (as seen in Fig. 10) with a rounded cluster in one corner of the depression. (b) is the InP surface after the In clusters have been removed chemically. This image illustrates the evolution of the shape as after the cluster retracts from the rectangular base the etching begins again under the new round cluster.

Until the current study, however, there was one significant difference between the Ga/GaAs and In/InP systems: the competition between coalescence growth of clusters and the etching of the substrate below the clusters led to non-partial spherical cluster shapes in the case of InP, a feature not observed in GaAs.

This observation is important, because the same physical processes should yield similar behaviour. The observations in the case of InP established not only that the etching processes below the clusters can lead to non-spherical cluster shapes, but also established a cyclic process, in which an initially round cluster resumes a stretched rectangular-based shape and then snaps back toward a rounded shape. This cycle was seen for certain large clusters at least to have been traversed twice during the time of the experiment (10 min).

This observation is fundamentally important in that a similar cycle has been observed in another Group III–V semiconductor system and thus the shape cycle is seen to occur not as an isolated phenomenon but as part of a non-linear nonequilibrium thermodynamic physical process.

5. Conclusion

We have presented an experimental study of cluster growth of Ga on GaAs(100). A shape cycle has been observed and is a result of subcluster etching where faster loss of material through a cluster results in an underlying depression. The subcluster etching further introduces another length scale in the system which causes the breakdown in self similarity on the cluster size and spatial distributions.

Acknowledgement

The authors gratefully acknowledge the support of NSERC.

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