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**Morphology, strain and composition of quantum dots**

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Keywords (user supplied):	quantum dots



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## The interdependency of morphology, strain and composition in buried GeSi/Si(001) quantum dots

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The deposition of Ge onto Si leads to the epitaxial growth of islands with varying morphologies. The size, shape and composition of the islands are all interdependent and change continuously during growth and overgrowth of the islands. A model of the morphological changes is presented which explains various shape changes observed during overgrowth by taking into account a dynamic equilibrium between the islands, the substrate and the wetting layers.

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Keywords: quantum dots; shape transformation; S-K growth;

### Introduction

The epitaxial formation of three-dimensional islands on a lattice mismatched substrate has attracted considerable scientific and technological interest for some time now.

The scientific interest arises from the complex nature of the process as much as the

insights it gives into phenomena as diverse as the strain relaxation in semiconductors

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[1, 2] and the initial stages of oxidation of copper [3]. Its technological interest

mainly stems from the potential applications of the islands as quantum dots in

electronic or optoelectronic applications [4, 5, 6]. One of the most extensively studied

systems is the formation of islands during the deposition of Ge on Si (e.g. [7, 8])

both, because of the importance of silicon and germanium in the semiconductor

industry and because this is a suitable model system to understand similar processes

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in more complicated compound semiconductor materials.

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This paper focuses on the morphological evolution of these islands. The aim is to clarify how the final island shape is determined by the interaction of the islands with the substrate, the intermixed planar layers (wetting layer) between the islands and any material that may be deposited subsequently onto the sample. To this end the paper draws on results of the existing and in parts contradictory literature to arrive at a comprehensive picture of the morphological development of the islands that takes into account both thermodynamic and kinetically driven processes.

While the basic mechanisms behind the transformation from planar growth to three dimensional island growth have been known for at least 50 years [2], the added complexities in the case of Ge islands on (001) oriented Si surfaces were first discussed in Refs. [7] and [8]. As in the most general case of the so called, Stranski-Krastanov growth, the growth in the Ge/Si system starts with a small number of planar Ge layers, which intermix with the underlying Si substrate. As more Ge is deposited the number of layers and their Ge content increases until a certain critical composition and layer thickness [9]. Then small pyramid shaped islands form which are bounded by {105} type facets (pyramid facets). As the island grows it changes shape from a pyramid to a more rounded dome-like shape and steeper facets are incorporated (dome facets) [7,8].

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### Shape transformation and reverse shape transformation

This shape change is a result of a competition between the surface area that is added by the island and the strain energy that is reduced by introducing steeper facets. Any formation of facets on a flat surface *increases* the surface area and therefore the surface energy in the system. However, in the case of Ge on the lattice mismatched Si

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it also *decreases* the strain energy. The critical pyramid size at which the steeper dome facets are introduced depends strongly on the island composition [10]. The higher the average germanium content in the island, the earlier the dome facets appear. The average Ge content is not only a function of the composition of the deposited materials, Si from the substrate diffuses into the islands to relieve the strain at the island – substrate interface and this can lead to significant non-uniformities in the composition throughout the islands. In fact, experimental studies [11] have shown that the content near the island-substrate interface can be below 35% when at the same time the top of the island is almost pure Ge.

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Increasing strain between the island and the substrate leads to the nucleation of steeper facets and therefore to a shape transformation from a pyramid to a dome shaped island. Interestingly, a “reverse” transition from dome to pyramid has been observed [12, 13] when Si was deposited on an as-grown Ge island. This is also technologically important since, to exploit the quantum confinement properties, the islands have to be embedded in a matrix material. This is usually achieved by switching from the precursor gas which induces island growth (e.g. digermane) to a gas which deposits more of the substrate material (e.g. disilane). However, since this deposition is generally carried out under similar conditions as the island growth, material deposited on top of the island can interdiffuse with the material in the island in much the same way as the substrate material does. In the case of Si deposition onto a Ge island, the diffusion of Si into the island is driven not only by the reduction of the strain energy but also by the fact that the surface energy of Si on Ge is considerably higher than Ge on Si. Above a certain amount of Si diffusion into the island, the strain energy may be reduced to such a degree that the steep facets are no

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2 longer energetically stable. Statistical studies of Ge/Si islands before and after the  
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4 deposition of a few monolayers of Si have led to the conclusion that the islands  
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6 indeed undergo a reverse shape transformation from domes to pyramids [12]. Ref [13]  
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8 showed that some islands shrink while they undergo a reverse shape transformation.  
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10 Other islands, particularly large ones, dissolved completely before they can be  
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12 embedded in the matrix. This is counterintuitive because of the fact that material is  
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14 deposited on top of the island and one would therefore expect an increase of the island  
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16 size depending on the amount of material added.

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19 In reality, the equilibrium shape of the island is determined not only by the  
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21 energy in the island itself but also by the energy of the whole system made up of all  
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23 islands and the wetting layer. That there is thermodynamically driven interaction  
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25 between different islands has been shown before when it was found that larger islands  
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27 grow at the expense of smaller ones (Ostwald ripening) [8]. To understand the  
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29 behaviour of this system it is important not only to look at processes in the individual  
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31 islands but also take into account the effect the Si deposition has on the wetting layer  
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33 and consider the islands and the wetting layer as a closely coupled system.

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37 This is reasonable as they are closely coupled even during the island formation. Yu et  
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39 al. [9] showed that in the initial stages the wetting layer forms by interdiffusion of the  
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41 deposited Ge and Si. As more Ge is deposited, the Ge content in the top layers  
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43 increases. Ge atoms do not generally penetrate deep into the surface of the substrate  
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45 as shown by Migas et al. [14]. They tend to stay confined within the top four atomic  
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47 layers. At a certain critical Ge composition the strain energy becomes high enough so  
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49 that island formation becomes energetically favourable. At this stage, any atoms  
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51 deposited onto the wetting layer either diffuse on the surface to attach onto an existing  
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2 island or, by binding to other atoms diffusing on the surface, form a new island. The  
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4 islands therefore not only grow by adsorbing atoms directly from the vapour phase  
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6 but also by capturing atoms which diffuse on the surface. Even coordinated  
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8 movements of whole islands are possible by atoms preferentially detaching from one  
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10 side of the island and attaching to the other side [15]. As the area on the sample  
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12 surface which is covered by islands is usually considerably smaller than the  
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14 uncovered area of the wetting layer between islands, the island morphology and the  
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16 morphological development is in large part determined by the interaction between the  
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18 island and the wetting layer.  
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21 It is important to realise that this strong coupling between the wetting layer  
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23 and the island morphology does not end when the growth conditions are changed so  
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25 that instead of Ge, Si is deposited in order to cap the islands. As Si is deposited onto  
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27 the wetting layer, it intermixes with the Ge top layer. This however disturbs the  
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29 equilibrium between a wetting layer and the islands and the Ge content in the wetting  
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31 layer falls below the critical composition. As a consequence, the wetting layer is  
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33 ready to take up any Ge atoms that detach from the islands. This is  
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35 *thermodynamically* favourable because the wetting layer relieves strain without  
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37 increasing its surface area. As a result, island composition shifts towards being more  
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39 Si rich. At the same time, the island loses material to the wetting layer. If atoms  
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41 migrate from the island into the wetting layer faster than Si atoms are being deposited  
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43 onto the island, the island volume shrinks. Because of the change in composition as  
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45 well as in size, the steep facets are no longer stable. Thermodynamically this favours  
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47 a reverse shape transformation from a dome to a pyramid shape.  
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### The kinetic pathway to the thermodynamically favourable morphology

Essentially, while the “target shape” of the island is energetically determined, the pathway to this shape has to be kinetically feasible. The kinetics of the system depends strongly on the availability of both Ge and Si at the surface since surface diffusion is a much faster process than bulk diffusion. The shape transformations of the island depend therefore strongly on the composition profile within the island and not only on the overall energy of the system. Some areas, especially Si rich areas far away from the island surface are essentially immobile whereas areas close to the island surface that are Ge rich play a strong role in the shape change.

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As outlined in [13], at sufficiently high temperatures and slow growth rates islands do indeed lose volume and revert to the pyramid shapes. For this to happen Ge atoms have to diffuse from the island surface into the wetting layer. While the island surface is expected to be Ge rich due to the lower surface energy of Ge, the supply of Ge from the bulk of the island is slow due to the much lower rate of bulk diffusion compared to surface diffusion. As discussed above, the apex of the island can be expected to be very Ge rich whereas a significant amount of Si would have diffused into the bottom of the island. It is therefore reasonable to expect that the top of the island is preferentially redistributed whereas the lower half remains intact for longer. As outlined in figure 1, this can lead to two very different kinds of shapes, depending on the respective lengths of the steep (dome) facets and the shallow (pyramid) facets. If the pyramid facets are longer or about equal to the length of the dome facets, the transformation from the dome shape to the energetically more favourable pyramid shape can be achieved by rearranging only the surface atoms, mainly from the top half of the island which has a high Ge content. If however the

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3 pyramid facets are short compared to the dome facets, the material in the pyramid is  
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5 not enough to transform the steep, dome facet into a pyramid facet. The Ge rich top of  
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7 the island is consumed before the transformation is completed and a flat top is left  
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9 behind, transforming the island into what can be described as a truncated pyramid. As  
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11 the rest of the material in the island is only accessible through the surface, material is  
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13 removed at a fairly large rate from the top facet. This can lead to dissolution of the  
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15 island without the island ever achieving the equilibrium pyramid shape.

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18 To illustrate this, figure 1 shows schematics of two possible island shapes, the  
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20 composition distribution within them and their projected development throughout the  
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22 Si deposition process. Figure 2 shows all the different diffusion processes that take  
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24 place at different points in the transformation. The in-situ TEM images below the  
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26 schematics (recorded using the equipment and conditions described in [13]) show a  
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28 real life example of shape transformation similar to the one in the schematics.

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30 However, it needs to be pointed out that the composition distribution in the islands  
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32 cannot be determined from the TEM images. The two islands which at the start of the  
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34 Si deposition have different lengths of dome and pyramid facets undergo very  
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36 different transformations during the Si deposition even though they followed the same  
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38 pathway of shape transformations during their formation. The island in figure 1 (a) is  
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40 at an earlier stage in the transformation and therefore smaller than the island in figure  
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42 1 (b) with the dome facets being shorter than the pyramid facets (the images in figure  
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44 1 are scaled to show maximum detail and do not represent the correct size relationship

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46 ). The island in figure 1(b) has longer dome facets than pyramid facets. The  
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48 composition distribution shown schematically (not visible in the TEM images) is  
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50 chosen to be consistent with the arguments outlined above. When the Si deposition  
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2 starts, the Ge rich volume towards the top of the island (shown in light grey) is  
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4 redistributed first. That leaves the larger island with an essentially flat facet on top.  
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6 For Ge atoms in the centre of the island, the shortest path to the surface is to diffuse to  
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8 the flat top facet. Material is therefore transported from there into the wetting layer.  
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10 Rather than transforming into a pyramid the island expands its top facet, becoming  
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12 what looks like a truncated pyramid. Over the course of the Si deposition more  
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14 material diffuses into the wetting layer until there is only a long flat mound left.  
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18 The island in figure 1(a) however does still have a high Ge content which is  
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20 highest at the island apex. Only the layers close to the island-substrate interface are  
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22 very Si rich. Ge atoms can therefore diffuse directly from the island surface to the  
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24 wetting layer. This gives also an easy pathway for material to be redistributed from  
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26 the island apex onto the short dome facets (figure 2), eventually flattening them and  
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28 enabling the island to transform to its equilibrium pyramid shape.  
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33 The mechanisms outlined above not only account for the in-situ observations  
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35 of Ge/Si islands in [13] but also for ex-situ observations of capped islands in other  
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37 materials systems which are predominantly found to have truncated pyramid shapes  
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39 [e.g. 16] which are not usually observed in uncapped islands.  
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### 42 43 Conclusions

44 To summarise, the island size, shape and composition before the capping process is  
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46 crucial for its morphological development during the capping. During the capping  
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48 process, the islands become essentially a reservoir of Ge for the wetting layer, much  
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50 like the wetting layer is a reservoir supplying Ge atoms to the islands during their  
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2 formation process. As the redistribution of Ge atoms from the islands to the wetting  
3 layer largely depends on surface diffusion, the largest amount of material is removed  
4 from the Ge rich apex of the islands. As the composition distribution in the island is  
5 strongly linked to island shape which in turn is determined by its size, one can  
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10 conclude that the evolution of island shapes during the capping process is a function  
11 of island sizes before the capping process. Therefore, while any one individual island  
12 may follow a different pathway of shape transformation during its capping process  
13 than during the growth process the former can nevertheless be viewed as the reverse  
14 process of the later when the whole system consisting of all islands and the wetting  
15 layer is taken into account.  
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23 Acknowledgements: C.L. would like to thank F.M. Ross and S. Kodambaka for their  
24 kind support in performing the in-situ TEM experiments and acquiring the TEM  
25 images shown in Figure 1.  
26

27  
28 Figure 1. shows the relationship between the relationship between the island shape  
29 before and after the Si deposition process. (a) illustrates the case of an island with  
30 short dome facets and long pyramid facets with a highly non-uniform composition  
31 distribution containing a large volume of Ge rich material at the top. (b) shows the  
32 case of an island with long dome facets and short pyramid facets with a more  
33 homogeneous composition distribution.  
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36 Figure 2. shows the interaction of different diffusion processes which lead to the  
37 reverse shape transformation or even a complete dissolution of the island. Black  
38 arrows symbolise Si deposition, grey arrows surface diffusion and the intertwined  
39 black and grey arrows symbolise the exchange of material between the surface and  
40 the bulk.  
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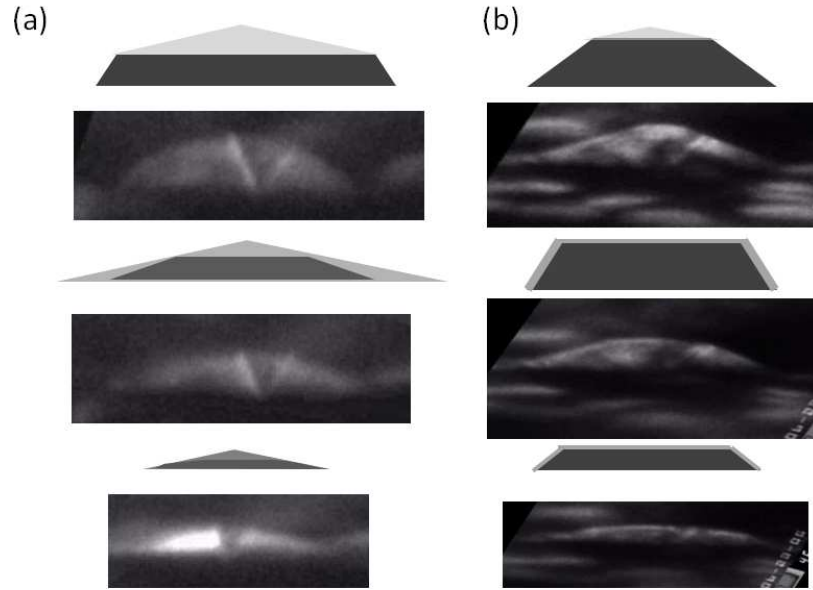


Figure 1. shows the relationship between the relationship between the island shape before and after the Si deposition process. (a) illustrates the case of an island with short dome facets and long pyramid facets with a highly non-uniform composition distribution containing a large volume of Ge rich material at the top. (b) shows the case of an island with long dome facets and short pyramid facets with a more homogeneous composition distribution.  
254x190mm (96 x 96 DPI)

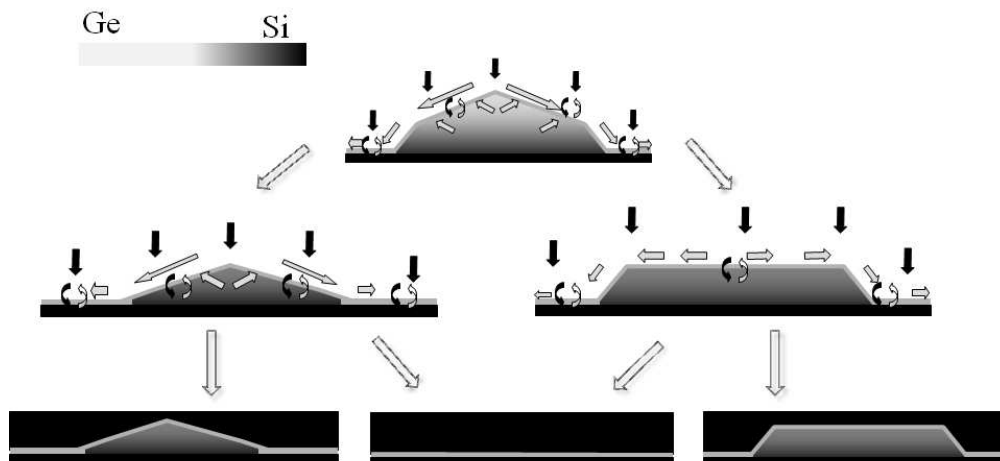


Figure 2. shows the interaction of different diffusion processes which lead to the reverse shape transformation or even a complete dissolution of the island. Black arrows symbolise Si deposition, grey arrows surface diffusion and the intertwined black and grey arrows symbolise the exchange of material between the surface and the bulk.

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3 Letter to referees:  
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8 I would like to thank both referees for their constructive comments. I have incorporated the changes  
9 suggested by referee 1 in the text. I am grateful to referee 2 for pointing out the mismatch between  
10 the scope of the paper and the title. I have tried to address this concern by changing the title of the  
11 paper to "The interdependency of morphology, strain and composition in buried GeSi/Si(001)  
12 quantum dots". While some of the concepts presented in the paper are applicable to quantum dot  
13 formation in other materials systems, this change in the title reflects the focus of the paper on the  
14 case of islands formed by depositing Ge and Si on (001) oriented Si substrates.  
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18 Referee 2 is correct to point out that for some surfaces and growth regimes no wetting layers are  
19 formed before the formation of the islands (e.g. Volmer-Weber growth). To avoid confusion I have  
20 added a comment in the introductory part, (p.2, line 12) which refers to the Stranski-Krastanov  
21 growth mechanism.  
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26 Other changes: I have added a short acknowledgements section at the end of the document (p. 9).  
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