Nanoscale Pit Formation at 2D Ge Layers on Si: Influence of Energy and Entropy

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The structural stability of two-dimensional (2D) SiGe nanostructures is studied by scanning tunneling microscopy. The formation of pits with a diameter of 2–30 nm in one atomic layer thick Ge stripes is observed. The unanticipated pit formation occurs due to an energetically driven motion of the Ge atoms out of the Ge stripe towards the Si terminated step edge followed by an entropy driven GeSi intermixing at the step edge. Using conditions where the pits coalesce results in the formation of freestanding 8 nm wide GeSi wires on Si(111).

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The structural instability of nanostructures during annealing is an important issue which, along with the compositional instability, can be a serious threat to the functionality of nanodevices. Since the diffusion energies and intermixing barriers are particularly low at surfaces, the stability of surface nanostructures is most delicate. In the GeSi heteroepitaxial system there is a strong thermodynamic driving force for intermixing, since intermixing reduces strain and increases entropy [1–3]. The evolution of heteroepitaxial nanostructures is complicated, since both morphology and composition determine the system energy [4]. Moreover, the system is often far from equilibrium due to kinetic barriers. From the experimental point of view the challenge is to supply a most complete data basis in order to be able to understand the evolution of the heteroepitaxial nanostructures, specifically simultaneous measurements of morphology and composition are desirable [5,6].

In the present Letter it will be shown that the driving force towards intermixing is so strong that it provokes drastic morphological changes during equilibration. These structural changes are a way to bypass the kinetic barriers for direct intermixing. In particular, we show that one monolayer (ML) high Ge stripes grown at Si(111) step edges are unstable towards pit formation during annealing. The Ge leaving the stripe during pit formation attaches at the (Si covered) Ge stripe and intermixes with the subjacent Si (Fig. 1).

The pit formation arises by a concerted action of processes driven by an energy gain of the system and processes driven by an increase of the entropy of the system due to intermixing. The question arises why this rather complicated mechanism of pit formation is followed instead of the much simpler direct vertical intermixing of Ge with the subjacent Si. We will show that while the direct intermixing process results in a final state of even lower energy as the final state after pit formation, the kinetic barrier involved is much smaller than the barrier for direct vertical intermixing which favors the pit formation.

In our experiments first a Bi terminated Si(111) surface was prepared by deposition of one atomic layer of Bi on the clean Si(111)-(7 × 7) at 875 K. Then a submonolayer amount of Ge was deposited at 655–675 K at a rate of 0.015 ML/min (1 ML corresponds to 1.56×10^{15} atoms/cm^2). During Ge growth the Bi floats up at the surface as usual in surfactant mediated growth [7,8]. In the following we will not mention that the complete surface is always terminated by one atomic layer of Bi. After submonolayer deposition, the Ge atoms attach to the step edges and form Ge stripes [Fig. 1(a)]. Atomic layer high (~3.2 Å) stripes with a width of more than 10 nm can be formed without any pit formation. Ge islands also grow more distant from the step edges. It was found that the

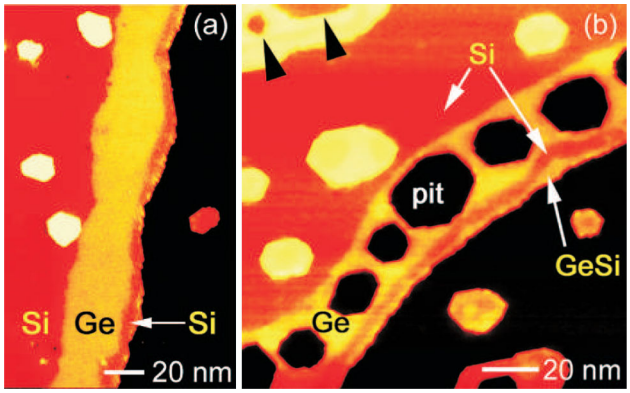

FIG. 1 (color online). (a) STM image of a one atomic layer high Ge stripe grown at a Si step edge. After Ge deposition a thin outer Si rim was grown. The apparent height contrast between Si and Ge is induced by the Bi termination of the whole surface. (b) After annealing at 733 K, unanticipated formation of pits and motion of the Ge originating from the pits to the outer Si rim is observed.

apparent height measured in STM is ~1 Å higher on Bi terminated Ge areas compared to Bi terminated Si areas, allowing a distinction between Si and Ge on the nanoscale [9]. For a GeSi mixture, the apparent height is a measure of the Ge concentration in the surface layer [6].

While attempting to grow alternating two-dimensional GeSi superlattices [10], we observed the formation of pits inside of Ge stripes for certain growth conditions. The formation of one atomic layer deep pits is pronounced if the growth of a sufficiently wide ($\geq$5 nm) Ge stripe deposition is followed by the deposition of a Si stripe and subsequent annealing. Pit formation was observed, for example, after the following growth sequence: 0.23 ML Ge was grown at $T = 675$ K, followed by 0.045 ML Si at 675 K before annealing for 10 min at 735 K. The STM image in Fig. 1(b) shows the resulting structure including 10–20 nm wide pits formed in the Ge stripe. The pit formation occurs by the same mechanism also at isolated Ge/Si islands (Ge core surrounded by a Si rim) on terraces far from the step edge, as indicated by the arrow heads in [Fig. 1(b)]. The material in the outer GeSi step edge is less than the missing material in the pits since some Ge attaches at Si islands also present at the surface.

In the following a model is described which explains the observed pit formation. In the first part of the pit formation process an initial amount of Ge is moving from the Ge stripe (pits) to the outer Si rim [Fig. 2(b)]. For simplicity we leave out the actual nucleation event. The driving force for the first part of the pit formation process is bond energy gain. Ge-Ge bonds present in the Ge area are replaced by stronger Si-Ge bonds [11–13] when Ge atoms attach to the Si terminated step edges. This process decreases the system energy and supplies an energetic driving force for Ge to form pits and to diffuse to the Si terminated step edge.

While the above reasoning can explain the initial pit formation, the pit formation should stop quickly if all Si step edges are terminated by Ge atoms [Fig. 2(b)]. Subsequent Ge attachment at the step edges would not result in any bond energy gain. A further growth of pits, as observed in the experiment, would not be expected because it would only increase the step energy. In a second step of pit formation the entropy driven GeSi intermixing acts at then outer step edge. The amount of GeSi intermixing can be close to 50% under usual conditions as obtained from the measured apparent height differences [6]. Because of the entropy driven intermixing at the step edge, Ge is trapped and fresh Si is present at the outer step edge again. This Si starts the energy gain driven Ge diffusion from the pits towards the Si containing step edge again [Fig. 2(b)]. The atomic processes shown in Figs. 2(b) and 2(c) can be considered as the subsequent energy driven and entropy driven parts of an energy–entropy cycle.

While we have shown that the above outlined pathway of pit formation describes the experimental data, we will now turn to an analysis of the free energy and kinetic barriers during pit formation. This will elucidate why an unanticipated, complicated process of pit formation is favored over the much simpler process of direct intermixing with the underlying Si [Fig. 2(d)] which has an even lower free energy than the final state of pit formation.

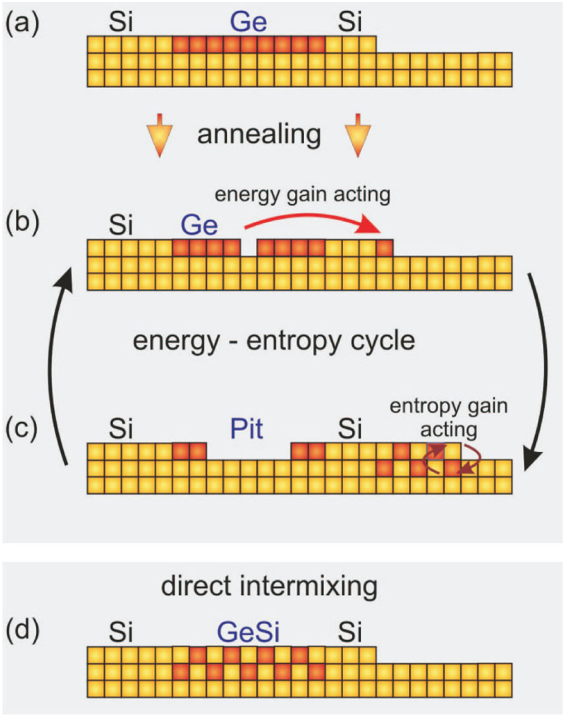

FIG. 2 (color online). In (a) and (c) the initial and final states before and after pit formation are shown. In the first part of the energy–entropy cycle (b) the energy is reduced by replacing Ge-Ge bonds (at the Ge stripe) through stronger Ge-Si bonds at the Si terminated step edge. The subsequent GeSi intermixing is driven by a gain in mixing entropy (c). Because of the intermixing, Ge is trapped and the Si at the step edge is (partly) restored activating the energy driven part of the cycle again. An alternative simpler intermixing process without pit formation is direct intermixing with the Si from the lower layer (d).

Since the pit formation occurs after annealing, we assume that the final state [Fig. 2(c)] with pits formed is a state close to local equilibrium. Since the system is a quite complicated heteroepitaxial strained partially intermixed system there are several contributions to the free energy. As the initial state we consider a Ge one monolayer thick stripe at a Si step edge and a thin Si rim at the Ge stripe [Fig. 2(a)]. The final state is the Ge stripe with one monolayer deep pits, the thin Si stripe, and an outer GeSi stripe consisting of the Ge originally filling the pits intermixed with the underlying Si layer [Fig. 2(c)]. For the amount of GeSi intermixing (x) in the outer GeSi stripe, we assume $x = 0.5$ which corresponds roughly to the experimentally observed range of intermixing. We consider here only intermixing at the surface since bulk diffusion does not operate at the temperatures and time scales used here due to the high activation barrier of 4–5 eV [14].

TABLE I. Free energy contributions for pit formation.

E_{elastic}	−17 meV/Ge atom
E_{mix}	+13 meV/Ge atom
mixing entropy	−88 meV/Ge atom
$E_{\text{step,rel}} + E_{\text{step,form}}$	−2– + 2 meV/Ge atom
$E_{\text{int,bound}}$	−3 meV/Ge atom

The free energy contributions for going from the initial to the final state were estimated and are shown in Table I.

As calculated from elasticity theory the elastic energy decreases by 17 meV/Ge atom in the final state due to the reduced strain in the outer intermixed GeSi stripe. Energy per Ge atom means per Ge atom moved away from the pits to the outside stripe. The mixing enthalpy of GeSi is known to be positive [15,16], resulting in a mixing energy of 10 meV/Ge atom, favoring the initial state without pits. The mixing entropy term gives a large negative contribution of −88 meV/Ge atom favoring the final intermixed state. A further contribution to the elastic relaxation energy is the step edge relaxation energy evaluated according to [17]. When this contribution is combined with the step edge formation energy which increases during pit formation a net step related energy gain is estimated and converted to of −2– + 2 meV/Ge atom (assuming an average pit diameter of 15 nm). This range is estimated from the extreme cases: zero step edge formation energy and the step energy of clean Si(111) [18]. The actual step formation energy on Bi terminated surface is expected to lie between this extreme cases. The last contribution to the free energy ($E_{\text{int,bound}}$) arises as follows: when the first Ge atoms move from the pits to the Si rim weaker Ge-Ge bonds are replaced (partly due to intermixing) by stronger Si-Ge bonds. We estimated this line energy and convert it again to an equivalent energy per (moved) Ge atom of about −3 meV/Ge atom.

Taking all the contributions to the free energy together the final state with pits formed has clearly lower free energy than the initial state. This seems to be a convincing energetic argument for the pit formation. However, let us now consider a much simpler final state, namely, the direct vertical intermixing of the Ge stripe with the underlying Si [Fig. 2(d)]. Most of the energy terms considered before apply to the vertical intermixed state as well. Only the step energies are not present because no steps are formed during direct vertical intermixing. Since this is a small contribution, the free energy of the direct vertically intermixed state is also lower than the initial state. Even more, the free energy of the directly intermixed state is lower than the final energy of pit formation since the intermixing would act at the whole Ge stripe, while the pits only form on a fraction of the stripe (usually less than one half).

The question arises of why the system takes the complicated pathway like the pit formation instead of the much simpler and lower free energy process of direct vertical intermixing with the underlying Si? During vertical intermixing high energy barriers have to be overcome in order to reach the low free energy configuration. The relevant barrier for direct vertical intermixing is the barrier for intermixing between the first and second layer which was recently measured for the Bi/Ge/Si(111) system as $U_{\text{ex}}^{\text{terrace}} = 2.2$ eV [6]. The corresponding barrier at the step edge is lower ($U_{\text{ex}}^{\text{step}} = 1.9$ eV) because the atoms are less confined by neighboring atoms at the step edges [6]. The pits are formed because pit formation allows a path towards the minimum free energy configuration which involves a lower barrier than the direct exchange path. Because of the decreased energy barrier for GeSi exchange at the step edge, entropy can act more easily at the step edge while on the terrace the lower entropy intermixed state is not realized due to the large energy barrier involved with the GeSi exchange at the terrace.

Now we turn to the question of why in the above described pit formation process the intermixing occurs only at the outer Ge stripe while it does not occur at the pit step edge? There is a kinetic reason for this. At the beginning of the pit formation the step length at the pits is much smaller than the length of the outer step. Therefore, the step speed at the pits is much larger than the step speed at the outer step. It is known that the GeSi exchange at the step edges depends critically on the step speed, being lowest at the largest step speeds [6] due to the shorter time a specific atom is located at the step edge. Therefore, the GeSi intermixing effect at the pits is initially much smaller than the intermixing at the outer GeSi step edges. When the pits grow larger their step speed reduces and GeSi intermixing starts to occur at the pit step edges as well. This is also the reason why the pits stop to grow at some point. The energetic driving force for pit formation disappears when the Si content at the pit step edge becomes close to the Si content at the GeSi stripe.

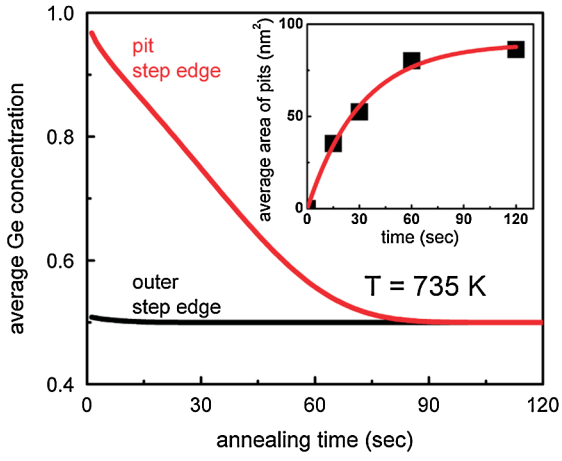

FIG. 3 (color online). Average Ge concentration at the pit step edge and at the outer GeSi step edge as a function of annealing time. The pit size measurements are shown in the inset.

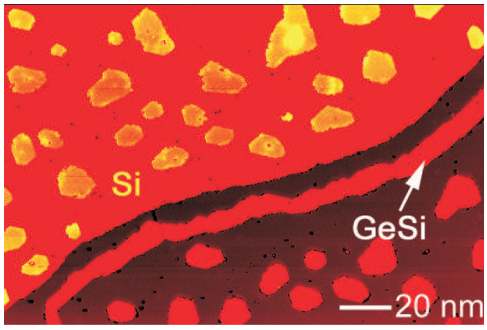

FIG. 4 (color online). Fabrication of a freestanding 8 nm GeSi wire on the Si(111) substrate obtained by pit coalescence.

A measurement of the average pit area as function of annealing time shows that the pit formation stops after about 90 sec (inset in Fig. 3). From a fit to this time dependence the average step speeds of the pits are calculated by differentiation. Furthermore, using the data on the Ge concentration at step edges as a function of step speed [6] we obtain the average Ge concentration at step edges plotted in Fig. 3 as a function of annealing time. Initially the difference in Ge concentration at both kinds of step edges, which is the driving force for pit formation, is large. For longer annealing times this driving force reduces and leads finally to a stop in further pit growth. An additional effect, not considered here, is that Si accumulates at the pit step edges due to the out diffusion of Ge which is another mechanism for the decrease of the Ge concentration with time.

Effective pit formation occurs only in a certain temperature range. For too low temperatures the GeSi exchange is not activated and the pit formation stops quickly after all Si steps have been terminated by Ge. For too high temperatures the difference in Ge concentration between both types of step edges, vanishes due to strong intermixing and the corresponding chemical potentials become the same.

The pit formation can be also used for nanostructuring. Using conditions at which pit formation is enhanced the fabrication of freestanding GeSi stripes with single digit nanometer width is possible. The sinks for the Ge during pit formation are Si step edges. In order to enhance pit formation we guided epitaxial growth in a way that a lot of Si islands were nucleated on the surface (0.08 ML Ge was grown at $T = 693$ K for 6 min, followed by 0.22 ML Si grown at 653 K for 14 min before annealing for 10 min at 753–773 K.). These Si islands provide a high density of sinks in order to drag the Ge out of the pits and finally leading to pit coalescence. Figure 4 shows an example of nanostructuring by pit coalescence. A continuous ~8 nm wide freestanding GeSi wire has been fabricated by pit coalescence. This wire is separated about ~8–10 nm from the step edge. Here the complete initial Ge stripe was removed. The Ge moved to the step edges of the Si islands and the GeSi stripe. Such nanostructured templates can be used for next stage nanostructuring, as in for instance anchoring molecular nanostructures selectively at the wire or in the groove between the step and the freestanding nanowire.

In conclusion nanoscale pit formation in 2D Ge stripes was observed due to a concerted action of energy and entropy. The energy driven motion of the Ge atoms out of the Ge stripe towards stronger binding sites at the Si terminated step edge is followed by an entropy driven GeSi intermixing which restores a Si content at the outer step edge and fuels the energy driven process again. This unanticipated complicated pathway of pit formation as a way to reach the final state of GeSi intermixing is followed instead of the much simpler direct vertical intermixing due to the high kinetic barriers present for the latter process. Finally we have shown that the pit formation effect can also be used for nanostructuring ~8 nm wide freestanding GeSi nanowires on the Si substrate.

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