Identification of Ge/Si Intermixing Processes at the Bi/Ge/Si(111) Surface

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The chemical contrast between Si and Ge obtained by scanning tunneling microscopy on Bi-covered Si(111) surfaces is used as a tool to identify two vertical Ge/Si intermixing processes. During annealing of an initially pure Ge monolayer on Si, the intermixing is confined to the first two layers approaching a 50% Ge concentration in each layer. During epitaxial growth, a growth front induced intermixing process acting at step edges is observed. Because of the open atomic structure at the step edges, relative to the terraces, a lower activation barrier for intermixing at the step edge, compared to the terrace, is observed.

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Interface abruptness in semiconductor hererostructures is a subject important for electronic device fabrication [1]. This issue becomes even more severe on the nanoscale. Already modest intermixing can be a thread for the stability and functionality of nanostructures composed of different materials. For the important Ge/Si system, intermixing has been studied intensively. However, at the surface, it has been notoriously difficult to measure the Ge/Si composition [2–7]. Nevertheless, there exists experimental [2–6] and theoretical [8,9] evidence that for Ge/Si(001) the intermixing occurs already at modest temperatures. Also, the use of a surfactant layer floating during growth was proposed as a way to suppress intermixing [10,11]. For a study of fundamental Ge/Si intermixing processes on the nanoscale, it is important to use a method with both high spatial resolution and chemical sensitivity which is difficult to achieve simultaneously [12,13]. Previously, we have found that it is possible to distinguish between Si and Ge at a Bi terminated surface by an observed apparent height difference in STM images [14,15]. Here, we exploit this for a quantitative study of Ge/Si intermixing.

We show that during annealing of a monolayer of Ge, the intermixing with the underlying Si substrate is confined to the first two crystalline layers (as long as bulk diffusion is negligible). During Ge growth, another intermixing process, growth front induced intermixing, acting at step edges is identified. For each particular Ge atom, this intermixing channel is open only for a short time when the atom is exposed at the step edge position, thus making the Ge concentration dependent on the step speed. In general, our study shows how a Bi termination can be efficiently used to suppress Ge/Si intermixing, enabling the fabrication of Ge/Si nanostructures in the one-digit nm scale.

In our experiments, a Bi terminated Si(111) surface was prepared by deposition of one atomic layer of Bi on the clean Si(111) − (7 × 7) at 740 K [14]. Then a submonolayer amount of Ge (1 ML corresponds to 1.56×10^{15} atoms/cm^2) was deposited at 700–755 K at a rate of 0.2 ML/min. During Ge growth, the Bi floated up at the surface as usual in surfactant mediated growth [10]. A flux of Bi (1 ML/min) was maintained during Ge growth to keep a complete Bi termination. Upon the growth, the surface was imaged at room temperature with STM at a constant sample bias of +3 V.

In the step flow growth mode, Ge atoms attach to the step edges so that monolayer thick Ge stripes form at Si steps. The Ge areas at the Si steps can be identified by their larger apparent height compared to the Si areas (Fig. 1(a)).

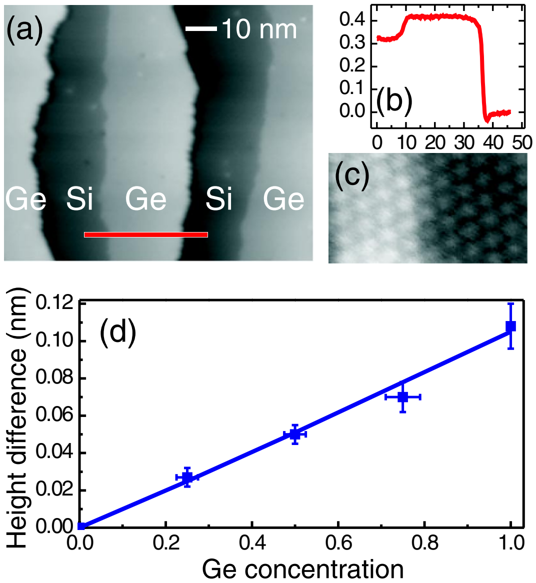

FIG. 1 (color online). (a) Apparent height difference between one atomic layer thick Ge stripes at the step edges (bright areas) and the Si terraces (darker areas). (b) Line scan (in nm) across the line in (a) showing the ~0.1 nm height difference between Si and Ge areas. (c) Atomically resolved STM image showing the Si/Ge border. (d) Calibration curve for the Ge concentration in the first monolayer against the measured height difference showing a linear behavior.

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The line scan across the Ge/Si boundary and a step edge is displayed in Fig. 1(b). The measured height difference of ~0.1 nm is a quite large effect. The atomic resolved image in Fig. 1(c) shows Bi trimers with a larger apparent height over Ge areas than over Si areas. It should be emphasized that the observed height difference does not result from real structural displacements of the atoms, but is an electronic effect [16].

The apparent height of Bi trimers depends on the local composition of the surface layer, i.e., on the number of Ge and Si atoms residing below a Bi trimer. If the first layer consists of a Ge/Si alloy, trimers of different heights are observed. In large scale images, a hardware average of the different apparent heights of the trimers yields a height difference characteristic for the given Ge concentration in the surface layer. To obtain a calibration of the apparent height difference for different Ge concentrations, we performed Ge/Si alloy deposition with Si and Ge deposition rates determined by a quartz crystal balance. The calibration experiments were performed at 700 K and a grow rate of 0.2 ML/ min. As will be shown later, under these conditions, one may neglect Ge/Si intermixing during growth, and the surface composition is determined simply by the fraction of Ge(Si) in the deposition flux. The results displayed in Fig. 1(d) show a linear dependence of the measured apparent height difference (between pure Si and Ge rich areas) as a function of the Ge concentration resulting in a calibration factor of 0.11 nm per ML. If, due to intermixing, Ge is present not only in the surface layer but also in the layer below the surface (second layer), this has also an influence on the measured apparent height difference. The calibration of the height difference for Ge present in the second layer was determined to be 0.035 nm per ML Ge [17]. Moreover, it was found that the second layer contribution to the height difference is independent of the chemical nature (Si or Ge) of the first layer and additive to the first layer contribution. The contribution from the third layer was found to be 0.02 nm per ML Ge.

First, we will analyze the intermixing of a deposited Ge monolayer (terminated by Bi) with the underlying Si substrate. Using the same procedure and deposition conditions as in the calibration experiments, we grew monolayer thick Ge stripes at Si step edges and then annealed the sample. Line scans across the border between the Si and Ge (rich) areas are shown in Fig. 2(a) for different annealing times ($T = 700$ K). The observed decrease of the apparent height difference indicates Ge/Si intermixing. As can be seen from Fig. 2(b) the measured height difference (corresponding via the calibration to a certain amount of Ge at the surface cf. the right axis) decreases exponentially with time, strongest for the highest annealing temperatures. Interestingly, the apparent height difference does not decrease to zero for large annealing times, as one would expect if Ge would diffuse into the bulk.

The finite value of the apparent height difference Δh for long annealing times indicates that a fraction of Ge remains close to the surface. The saturation value of Δh, and, accordingly, the equilibrium composition of the surface and subsurface layers, are temperature independent. This means that there is no significant energy gain for the place exchange between Si and Ge, and the Ge/Si intermixing is driven solely by the mixing entropy. To confirm this, we have performed density functional theory calculations of energetics of structures with different compositions of the first two crystalline layers. The calculations have been carried out using the Vienna *ab initio* simulation package (VASP) with projector augmented-wave pseudopotentials and generalized gradient approximation [18]. Calculations have shown that the energy difference between the nonintermixed (Bi/Ge/Si/Si...) and intermixed (Bi/$\mathrm{Ge}_x\mathrm{Si}_{1-x}$/$\mathrm{Ge}_{1-x}\mathrm{Si}_x$/Si...) structures is indeed very small. For instance, when one third of Ge goes to the second layer ($x \approx 0.33$), the total energy of the system increases only by 0.01 eV per $\sqrt{3} \times \sqrt{3}$ unit cell. At $x \approx 0.66$, one gets a bit larger value of 0.08 eV, which is still a relatively small effect.

Since the maximum of the mixing entropy is attained when the Ge is equally distributed among the layers par-

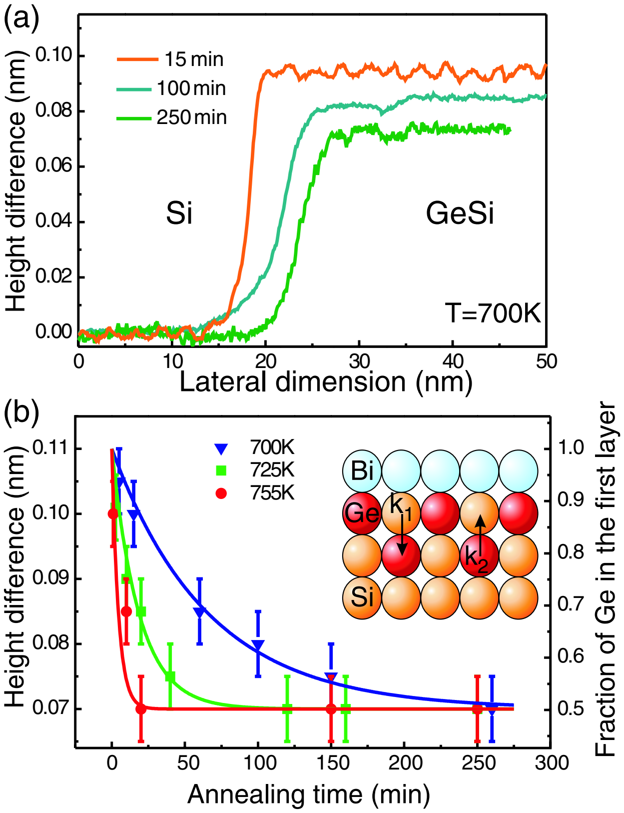

FIG. 2 (color online). (a) Line scans of the apparent height difference between Si and a deposited area of (initially) pure Ge (one ML thick) for different annealing times ($T = 700$ K). The decrease of the apparent height as function of time is indicative of vertical Ge intermixing with Si. (b) Measured height difference as function of annealing time for three different temperatures. The height difference saturates at a nonzero value indicating that Ge does not diffuse into the bulk. The solid lines are theoretical curves obtained with a two-layer intermixing model.

ticipating in the intermixing process, one would expect complete dissolution of the Ge in the Si matrix. However, kinetic constraints could prevent penetration of Ge atoms deep into the Si at finite temperatures. For instance, the bulk Ge diffusion (activation barrier 4–5 eV) [19] does not operate at the temperatures and times used here. Close to the surface, the kinetic constraints may be not so strict because atoms there are less confined and paths for Ge/Si intermixing with considerably lower activation barriers are expected [2]. If only the two topmost layers are involved in the intermixing process, one would expect a 50% Ge concentration in the first and second layers. An easy check shows that this surmise is in a perfect agreement with the experiment. Using the calibration relation $\Delta h = 0.11n_1 + 0.035n_2 + 0.020n_3$ with equal Ge concentrations in the first two layers ($n_1 = n_2 = 0.5$), and no Ge in the third layer ($n_3 = 0$), one obtains $\Delta h = 0.07$ nm, exactly the value measured in the experiment. Thus, we conclude that during annealing of an initially pure Ge monolayer on the Bi-covered Si(111) surface, the intermixing is confined to the first two layers yielding a 50% Ge concentration at equilibrium. This is different from the Ge/Si(001) system where up to four topmost layers participate in the intermixing process and the equilibrium Ge concentration varies from layer to layer [2].

Regardless of the atomic-scale pathway of the Ge/Si intermixing, one may consider the transition of an Ge atom from the first to the second layer as a thermally activated process which proceeds by overcoming of an energy barrier E_1 with a rate $k_1 = \nu \exp(-E_1/k_B T)$. Here, ν is the attempt frequency, T is the substrate temperature, and k_B is the Boltzmann constant. Similarly, the reverse process of the transition of a Ge atom from the second to the first layer may be associated with an *a priori* different energy barrier E_2 and a rate $k_2 = \nu \exp(-E_2/k_B T)$. Since the intermixing is confined to the two topmost layers, the evolution of the Ge concentration in the surface layer n_1 is described by a simple rate equation:

$$\frac{dn_1}{dt} = -k_1 n_1 + (1 - n_1) k_2. \tag{1}$$

The solution of this rate equation with the initial condition $n_1(0) = 1$ yields

$$n_1(t) = \frac{k_2}{k_1 + k_2}\left(1 + \frac{k_1}{k_2} e^{-(k_1+k_2)t}\right). \tag{2}$$

Knowing the Ge concentration in the first layer also determines the Ge concentration in the second layer ($n_2 = 1 - n_1$). Using the previously determined calibration, Eq. (2) was applied to fit the measured height differences. The result of the fit is shown in Fig. 2(b) as solid lines. The model fits the experimental data for all three temperatures using activation energies $E_1 \approx E_2 = 2.21 \pm 0.05$ eV and the attempt frequency ν of the order of 10^{12} sec^{-1}. This value for the activation energies in Ge/Si intermixing between the first and second layer lies reasonably between the bulk diffusion energy (4–5 eV) [19] and the surface diffusion energy around 0.7 eV [20]. The fact that the activation energies (which are *a priori* different) are the same within the error bars can be explained by our *ab initio* calculations. The *difference* between the activation energies is just the difference between the equilibrium energies for Ge in the first and second layer, which the *ab initio* calculations predict to be very small. Since our model is not taking into account the actual intermixing pathways and diamond lattice structure, the obtained activation energies have to be considered as effective activation energies for the Ge/Si exchange between the layers.

The second intermixing process we will consider is an intermixing process happening during epitaxial growth at step edges (Fig. 3). The vertical intermixing we studied before happens over the whole area of a Ge stripe. However, at step edges, the Ge/Si intermixing might be easier than on the terrace. The atoms at the step edge have less nearest neighbors and more steric freedom for an exchange process. Therefore, a lower activation energy for exchange is expected at step edges. However, since during epitaxial growth the step edge sweeps over the surface, one particular atom can only for a short time participate in this specific exchange process. This time is of the order of a_0/v_s, where v_s is the step propagation speed and a_0 is the distance per atom on the Si(111) surface. Thus, one characteristic of this growth front induced intermixing is the dependence of the amount of intermixing on the step speed. The growth front induced intermixing will become stronger for slow steps due to the longer time this exchange channel at the step edge is available for a particular atom. This step-specific intermixing mechanism should not be confused with that observed in the Ge/Si(001) system, where spontaneous formation of pairs of opposite steps was found to facilitate intermixing

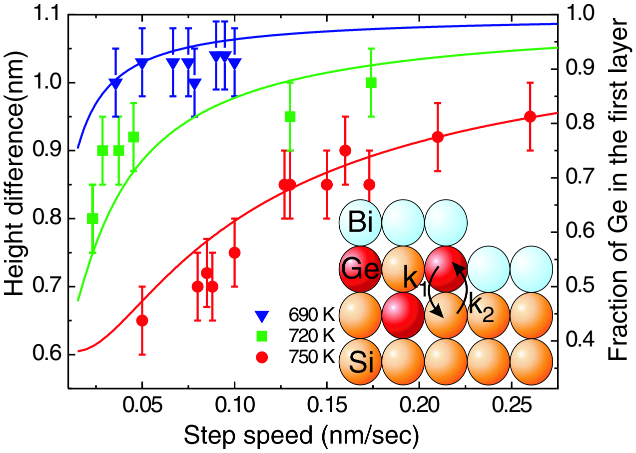

FIG. 3 (color online). Experimentally observed height difference as function of step speed for three different temperatures compared to the predictions of the model of growth front induced intermixing acting at step edges. A stronger intermixing (smaller height difference) is observed for slower steps (narrower Ge rich stripes).

by making a deeper subsurface layer accessible for Ge diffusion [3].

The step speed dependence of the apparent height difference was determined by measurements of the height difference for Ge rich stripes of different width. Because of variations of the interstep distances on the substrate, the Ge incorporation fluxes can vary locally being larger in areas of larger step spacing and smaller in areas where step edges are closer to each other. Since all the stripes on the surface are grown within the same deposition time τ, the local step speed v_s for each stripe width l_s is $v_s = l_s/\tau$. For narrower stripes (lower growth speed) a smaller height difference (stronger Ge/Si intermixing) is observed (Fig. 3). The measured apparent height differences for three different temperatures are shown as data points in Fig. 3. As a model for the Ge/Si intermixing at the step edge, we use again the intermixing between the first and second layer, however with different activation energies due to the different local atomic structure at the step edge. The Ge concentration can be determined again using Eq. (2), where the time t should be replaced by the inverse step speed a_0/v_s which characterizes the time before an atom at the step edge will be covered by the next incorporating atom and the growth front induced intermixing will be ceased for the covered atom. The model provides a good fit to the data for three different temperatures, so giving a hard evidence for the step-specific intermixing mechanism. From the fit, we obtain the following values for the activation barriers: $E_1(\text{step}) = 1.89 \pm 0.05$ eV and $E_2(\text{step}) = 1.92 \pm 0.05$ eV, which are equal within the error margins. The absolute values are lower than the exchange activation barriers on the terrace, which is expected as a consequence of the easier Ge/Si exchange at the open step edges.

We also studied the importance of the Bi termination on Ge/Si intermixing. In order to do this, we deposited Ge without Bi termination and tried to use Bi afterwards as a kind of "stain" to distinguish Si and Ge. However, in these "after-capping" experiments, we never found any height difference between Si and the expected Ge areas at the step edges. We think that the reason for this is a displacive adsorption of Ge on $\text{Si}(111) - (7 \times 7)$ [21], similar to that found in the case of Ge on Si(001) [22]. Displacive adsorption means that the Ge atoms impinging on the terraces exchange with Si so that a Ge/Si alloy is left behind on the terraces as well as at the step edges. This homogenous Ge/Si alloy present all over the surface naturally explains the absence of any apparent height difference (for instance at step edges) after capping with Bi. Thus, Bi is not just a stain to obtain chemical contrast between Si and Ge, but Bi termination is essential to suppress Ge/Si intermixing during the fabrication of Ge/Si nanostructures at the atomic level.

In conclusion, we studied Ge/Si intermixing at the Bi terminated Si(111) surface quantitatively. We found two modes of intermixing: First, a vertical Ge/Si intermixing confined to the first two crystalline layers, and second, a growth front induced intermixing acting at step edges. Experiment and model provide knowledge of the interface elemental profile after growth and annealing. The Bi is not merely acting as a stain but plays a major role in the suppression of Ge/Si intermixing and enables therefore the fabrication of self assembled Ge/Si structures on the one-digit nanometer scale.

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