PHYSICAL REVIEW B VOLUME 60, NUMBER 12 15 SEPTEMBER 1999-II

Surface electronic structure modifications due to buried quantum dots

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(Received 13 July 1999)

Coherently strained Ge islands have been grown on Si(100) substrates by means of molecular beam epitaxy and subsequently covered by a 10-nm-thick Si cap layer. *In situ* scanning tunneling microscopy revealed surface protrusions (up to about 0.4 nm) whose height depends on the size of the buried Ge dots. From the surface deformation, the in-plane strain within the capping layer was calculated. Evidence for directed diffusion of Si adatoms away from the highly strained regions was found. On the protrusions, a lowering of the surface band gap was measured using locally resolved scanning tunneling spectroscopy. This can be explained by changes of the electronic structure of the silicon surface induced by the inhomogeneous strain around the buried dots. [S0163-1829(99)51236-8]

One of the most interesting phenomena encountered in semiconductor physics during the last few years is self-ordered growth of nanoscale structures. Making use of the Stranski-Krastanow growth mode in lattice-mismatched semiconductor heteroepitaxy, the fabrication of arrays of small islands, acting as quantum dots, has become possible. The discrete energy spectrum of quantum dots renders them extremely interesting for the development of lasers and even for quantum computers.[1] For such applications, the dots must be embedded in a semiconductor matrix. The process of burying such small nanostructures by epitaxial growth turns out to be a nontrivial problem, however. As noticed by several researchers, the dots tend to change shape while the overlayer is grown, resulting in pronounced flattening.[2–5] In addition, the dots may change their composition and, as demonstrated for small Ge clusters, even dissolve completely.[5] The physical mechanisms responsible for these modifications appear to be related to the elastic strain relaxation of the dots and the surrounding matrix and to surface segregation (see, e.g., Ref. 4). Three-dimensional confinement of carriers can not only occur within the self organized islands, but also in the surrounding material, with the islands acting as stressors, modifying the band structure by their strain field. Such strain-induced quantum dots have been found to form in $In_xGa_{1-x}As$ quantum wells,[6] the local strain stemming from InP islands, grown on top of a thin GaAs cap. In stacked layers of carbon-induced quantum dots, the measured redshift of photoluminescence (PL) spectra was explained by electron confinement in the strained silicon above the Ge islands.[7] In the past, scanning probe methods have been used mostly to study the nucleation and structural aspects of quantum dot formation, with few exceptions, such as ballistic-electron-emission microscopy (BEEM), from which spectroscopic information on InAs dots has been obtained.[8] Very recently, cross-sectional scanning tunneling microscopy (XSTM) has been applied to InAs quantum dots embedded in GaAs and the strain in growth direction and the band gap of the InAs dot has been compared with the one of the GaAs matrix.[9]

In this paper, we present a scanning tunneling microscopy (STM) study on Ge dots embedded in a silicon film. Using our STM in the conventional configuration, we have measured the deformation of the silicon cap layer caused by the buried Ge islands. From the surface deformation the lateral strain above a quantum dot has been calculated. As will be shown below, scanning tunneling spectroscopy (STS) gave direct evidence for a lowering of the surface band gap in the strained parts of the Si cap, which could be correlated quantitatively with the lateral strain.

The samples used for this study were grown by molecular beam epitaxy (MBE). The oxide was removed from the lightly *p*-doped (7–12 Ω cm), well-oriented ($\pm 0.05°$) Si(100) wafers by thermal desorption. Subsequently a 240-nm-thick undoped silicon buffer layer was grown, exhibiting the usual 2×1 reconstructed surface as verified by reflection high energy electron diffraction (RHEED). 6 ML of germanium were deposited from a Knudsen cell at a rate of 4 ML/min while the sample temperature was kept at 500 °C. After a 5 min anneal at the growth temperature, the samples were cooled to 310 °C and 3 nm of silicon were deposited at a rate of 0.05 nm/s. Three additional 2-nm-thick Si layers were grown at 350, 390, and 470 °C. A final 1-nm-Si cap was grown at 550 °C. After a 5 min anneal at 550 °C, the wafers were cooled to room temperature and transferred to the STM chamber in UHV. The complicated procedure for the growth of the silicon cap layer was chosen in order to minimize Ge surface segregation and dissolution of the germanium islands, and at the same time to create a flat, well-ordered surface. By cross-sectional transmission electron microscopy (TEM), it was verified that the germanium islands were still present. A flattening of the islands was, however, apparent, and the formation of a SiGe alloy at the island boundaries or even in the core region seems most likely (see, e.g., Ref. 4). In Fig. 1, two equally sized STM topography images of one and the same sample are shown before [(a)] and after [(b)] the growth of the silicon cap layer. Before overgrowth, a bimodal island distribution[10] is found on the sample surface: hut clusters[11] (indicated by *H*)—some with quadratic base but most of them elongated—and domes (denoted by *D*). The latter are of similar base size, but two to three times higher due to their higher indexed side facets. Typical dimensions of the {105} facetted hut clusters are a width of 30–40 nm and a height of 3–4 nm, whereas the domes are between 6 and 10 nm high and feature {113} and

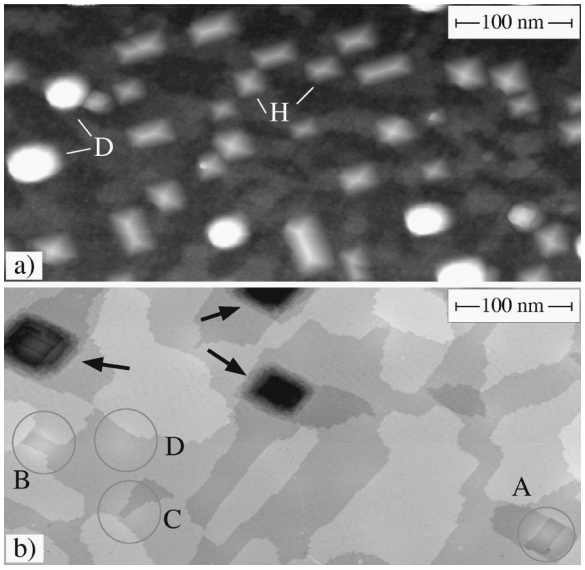

FIG. 1. (a) STM topography image of Ge islands grown on a Si(100) substrate at $T=500\,^{\circ}$C. Hut clusters (H) and domes (D) are present. (b) Topography image of the same sample after deposition of 10 nm of silicon. A surface protrusion is found at locations where Ge islands have been overgrown. In the deeper ''holes'' in the film (arrows) the surface distortion is largest, while it becomes gradually smaller at the locations surrounded by circles A, B, C, and D. The range of the grayscales is 6 nm and 1.7 nm in (a) and (b), respectively.

{102} as well as {105} facets. Figure 1(b) shows the sample surface after the deposition of 10 nm of silicon. Most apparent are the holelike features indicated by black arrows. Upon closer inspection, the sample surface can be seen to be bent upwards within such a ''hole'' [see, e.g., upper left corner of Fig. 1(b)]. The same kind of surface corrugation is found in regions surrounded by the circles in Fig. 1(b) and labeled A, B, C, and D for decreasing amplitude of the corrugation. As a matter of fact, many more very slight surface protrusions like the one indicated by D are found in the image. Their number density is comparable to the number density of the hut clusters determined before capping, i.e., $3.5\pm0.2\times10^{10}$ cm^{-2}. The density of the ''holes'' ($3.5\pm0.7\times10^{9}$ cm^{-2}) agrees very well with the number of domes, which were present prior to silicon deposition ($4.4\pm0.75\times10^{9}$ cm^{-2}). The maximum curvature of the surface was measured to be higher in the center of the ''holes'' than on the bumps present in the more planar regions (A, B, C, and D in Fig. 1). We can therefore conclude that larger Ge islands induce a larger outward bending of the growing surface, which in turn must cause higher lateral strain in the Si growing on top of the island. At higher temperatures, Si adatoms diffuse away from the strained parts of the sample surface[4] leading to the formation of ''holes.'' On top of the smaller Ge islands (hut clusters) the strain in the growing Si film is smaller and only step pinning (B, C, and D) is found to occur.

Figure 2 allows for a closer look at a surface region, where a Ge island of intermediate size has been overgrown. There are two incomplete terraces close to the center of the surface protrusion. The Si surface exhibits the same 4×2 reconstruction[12] close to the buried island and away from it.

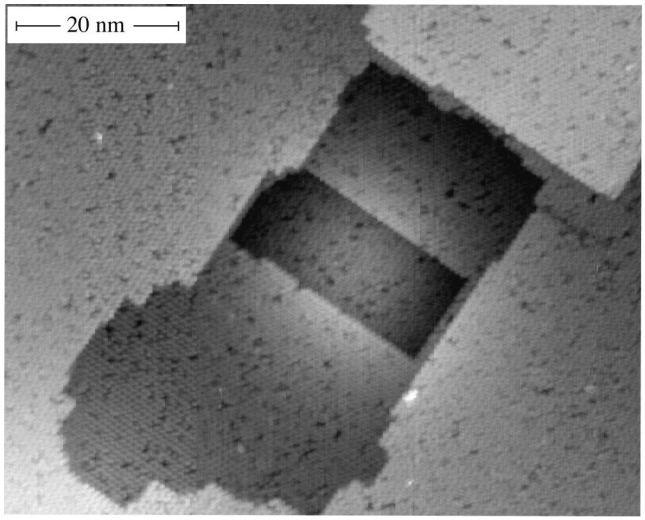

FIG. 2. STM topography image of a surface protrusion caused by a germanium island below a 10-nm-thick silicon cap layer. The grayscale range is 0.51 nm.

In order to analyze the deformation of the surface quantitatively, the monolayer steps have been removed from the image by masking out the regions belonging to the same terrace and adding an appropriate multiple of a monolayer step, $a/4$, to the measured height. Contour plots (not shown) made of the processed image indicate that the surface deformation has almost perfect circular symmetry. The same procedure was applied to other images, with the result that only a slight deviation from circular contours towards a rectangular shape (with the flat side along $\langle100\rangle$ directions) can be found for some regions. We take this as an indication that the elastic anisotropy may be neglected in a first approximation for strain modeling.[13]

A height profile, taken across the deformation peak in Fig. 2 and corrected for surface steps, is presented in Fig. 3. The height of the peak is 0.35 nm, more than twice as high as a monolayer step on Si! Most of the surface bumps are smaller: their height varies between 0.05 and 0.1 nm. Their cross sections were, however, found to be similar in shape to the one in Fig. 3. Using a model described below, the surface deformation, which would be expected for a Ge hut cluster

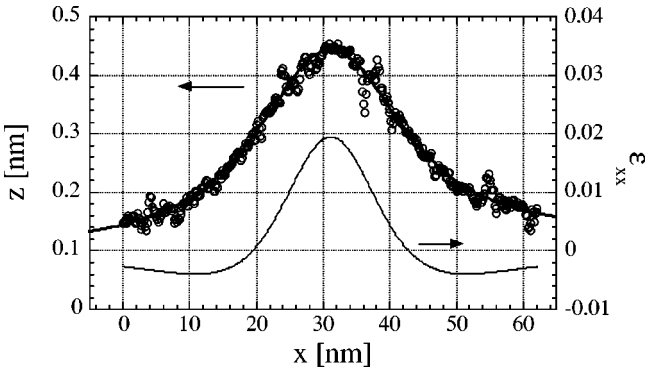

FIG. 3. Line section across the surface protrusion shown in Fig. 2 after subtraction of surface steps. A fit to a model describing the deformation of an elastic medium due to a point source is also plotted (continuous curve) along with the strain component ϵ_{xx} deduced from the fit (lower curve).

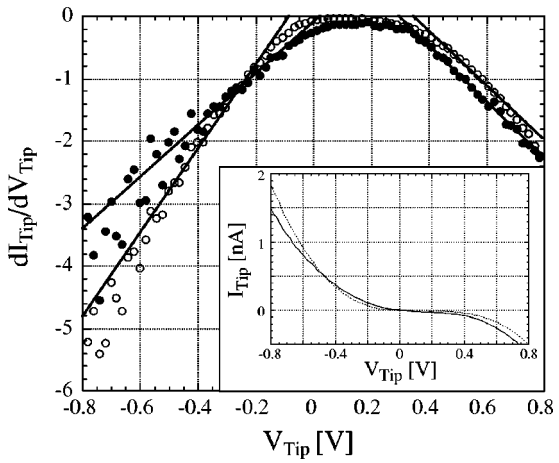

FIG. 4. Scanning tunneling spectra of silicon recorded above (●) and away from (○) a Ge island with the tip stabilized at $V_{Tip} = -0.5$ V and $I_{Tip} = 0.5$ nA. The original spectra are shown in the inset. The change in the surface band gap was calculated to 0.16 ± 0.03 eV from fits to the derivative of the spectra.

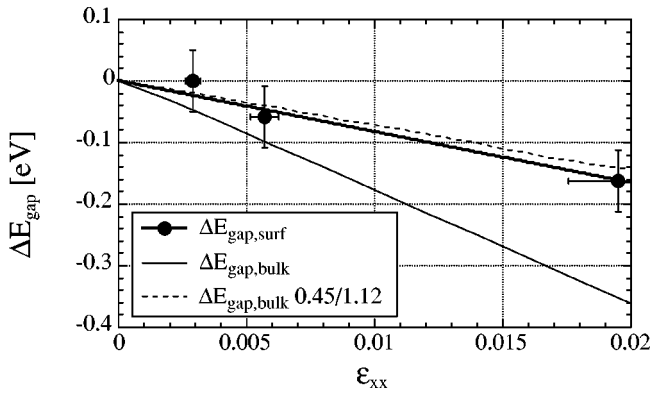

FIG. 5. Strain-induced lowering of the surface band gap measured with tunneling spectroscopy. The calculated lowering of the bulk band gap is also plotted. The dashed line gives the relative change of the bulk band gap multiplied by the measured surface band gap of 0.45 eV.

(approximated as a square based pyramid featuring 40-nm base length and 4-nm height), covered by 10 nm of Si, was calculated. The resulting surface deflection of 0.15 nm confirms that the island below the surface region shown in Fig. 2 featuring a protrusion of 0.35 nm is not a hut cluster, but a larger island of the dome type. The calculated deflection of 0.15 nm is, however, about two times bigger than the 0.05 nm until 0.1 nm measured for the vast majority of surface bumps, which were previously attributed to buried hut clusters. This can be explained by dissolution of Ge in the Si cap layer, which causes the buried islands to be significantly smaller than they originally were.[4,5] Additional evidence for the presence of significant island shrinking is provided by the fact that the largest domes, which were found to be higher than 10 nm before the overgrowth, resulted in the holelike features present in Fig. 1, after the deposition of only 10 nm of silicon. The actual islands embedded in the Si must, therefore, all be considerably smaller than 10 nm. This could be confirmed by the cross-sectional TEM measurements, where no islands higher than 4 nm were observed.

To calculate the surface deformation we used a model by Hu,[14] describing the displacement caused by a thermal inclusion in a semispace ($z \geqslant 0$). In an elastic medium featuring a Poisson's ratio ν, the displacement vector $\mathbf{u}^*$ at the position (x,y,z) caused by a point source of volume $dx'dy'dz'$ of a material with a lattice mismatch δ (here $\delta = 0.04$), located at (x',y',z') is given by

$$\mathbf{u}^* = \frac{\delta(1+\nu)}{4\pi(1-\nu)}\left(\frac{\mathbf{R}_1}{R_1^3} + \frac{(3-4\nu)\mathbf{R}_2}{R_2^3} - \frac{6z(z+z')\mathbf{R}_2}{R_2^5} - \frac{2\mathbf{k}}{R_2^3}[(3-4\nu)(z+z')-z]\right)dx'dy'dz', \qquad (1)$$

where $\mathbf{k}$ is a unit vector in z direction and $\mathbf{R}_1 = (x-x', y-y', z-z')$, $\mathbf{R}_2 = (x-x', y-y', z+z')$.

The surface distortion due to an embedded island can be found by integrating such point sources over the volume of the island (where $\delta \neq 0$). As mentioned before, this integration has been performed for a square based hut cluster with 40-nm base length. The surface was found to move upwards on top of the center of the island by 0.15 nm, which is about twice as much as the values measured for buried hut clusters. This discrepancy is the result of the island's change of shape during silicon deposition. As the exact island shape is unknown, we have tried to fit the surface profile using a single point source term [u_z^* in Eq. (1)]. The agreement is remarkably good (cf. Fig. 3). The parameters used to reproduce the surface profile (a volume of $dx'dy'dz' = 5452\,\mathrm{nm}^3$ and a depth of $z' = 16.57$ nm) cannot be directly interpreted as island volume and position. But it is possible, using these parameters, to determine the strain at the silicon surface. The strain tensor is readily obtained by differentiating Eq. (1). In Fig. 3 the ϵ_{xx} component of the strain tensor has been plotted. In the center of the island the tensile strain amounts to 0.02, half the value of the strain present in silicon epitaxially grown on a germanium substrate.

Having established the strain distribution in the Si cap above a buried dot, we are now in a position to have a look at the way in which the strain affects the electronic properties. Using scanning tunneling spectroscopy,[15] we recorded spectra on the part of the surface shown in Fig. 2. One of the two spectra plotted in the inset of Fig. 4 was obtained by averaging 132 spectra taken within a circular spot (diameter 10 nm) on top of the surface protrusion (●). The spectrum denoted by (○) is an average of 784 spectra stemming from an unperturbed surface region located in the upper left corner of Fig. 2. From the derivative of the spectra displayed in Fig. 4, the Si surface band gap was determined by fitting to a straight line close to the gap region.[16] It is evident that the gap is reduced for the spectra taken on the highly strained Si right on top of the covered Ge dot. For the unstrained silicon, the band gap was found to be 0.45 ± 0.05 eV, in agreement with theoretical calculations.[17] In the center of the surface deformation, the gap is lowered by 0.16 ± 0.03 eV because of the lateral tensile strain of 0.02. The states probed with negative tip bias, i.e., the conduction band states, are most affected by the strain. The same kind of analysis was carried out for islands causing a smaller surface distortion. The resulting differences in surface band gap are plotted in Fig. 5 as a function of maximum tensile strain at the dot center. The measured ΔE_{gap} vs ϵ values agree within the error with a

simple proportional dependency. The expected lowering of the bulk band gap (lowest conduction band minus highest valence band energy) of Si was calculated using the parameters from Ref. 18 and also plotted for comparison. The dotted line gives the variation in the surface band gap, expected on the assumption that the relative changes in surface band gap and bulk band gap are the same.

An intuitive understanding as to why the band gap of the surface states should be lowered in the presence of expansive strain, can be gained from the fact that the dimer bonds at the surface are stretched. This results in a smaller overlap of the two π orbitals of the Si dimers, which in turn causes the $\pi - \pi^*$ bonding-antibonding splitting to become smaller.

The strain distribution around islands embedded in a matrix material is of great interest. We have found evidence for directed diffusion of Si away from the strained surface regions on top of a buried Ge island. Directed diffusion of Ge towards regions with higher strain has been identified by Tersoff *et al.*[19] as the driving force for self-alignment of islands in stacked island multilayers.[20] In the case of stacked carbon-induced germanium-island multilayers in silicon, a spatially separated confinement for holes and electrons has been suggested recently[7] to account for a redshift in PL spectra. The strain-induced lowering of the Si surface band gap observed here, is in agreement with the idea of electron confinement in the strained Si close to an embedded Ge dot.

Financial support from the Swiss National Science Foundation (NFP 36) is gratefully acknowledged.

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[12] The surface reconstruction usually found on clean Si(100) surfaces at room temperature is 2×1. The buckling of the dimers, which results in a 4×2 reconstruction, is most probably induced by a small amount of Ge atoms segregated to the surface. We do not, however, find the 2×8 reconstructed surface dominated by vacancy lines, which is characteristic for a Ge-rich surface.

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[16] The spectra have also been evaluated by calculating $(dI/dV)/(I/V)$, a quantity which is proportional to the surface LDOS (Ref. 15). The spectral features are similar to those observed for a (2×1) reconstructed Si(100) surface [see, e.g., R. J. Hamers, Ph. Avouris, and F. Bozso, Phys. Rev. Lett. **59**, 2071 (1987)] and the change of the surface band gap as determined by the energy shifts of the π,π^* peaks next to E_F is in agreement with the value obtained by fitting dI/dV curves. Since smoothing had to be applied to the $(dI/dV)/(I/V)$ spectra, we prefer fitting the (unsmoothed) dI/dV curves.

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