Stress-Induced Shape Transition of $CoSi_2$ Clusters on Si(100)

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$CoSi_2$ clusters on a Si(100) surface grow in a square shape at first, but at a critical size a shape transition to clusters with large aspect ratios occurs. Each cluster is connected to an implanted layer of cobalt by a thermally induced defect that serves as a diffusion channel. In this novel growth mode the existing clusters can grow with a continuous supply of cobalt while cluster-cluster interaction is prevented from becoming a dominant factor to the cluster shape as a result of the large distance between defects. Our data are in good agreement with calculations on the balance between surface and interfacial energies on the one hand and stress relaxation due to an elastic distortion of the substrate on the other. [S0031-9007(98)05917-1]

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Rectangular hut clusters were first observed by Mo *et al.* [1] during the initial stages of Ge growth on silicon where the strained layer releases tension by creating a saw-toothed surface with very flat structures (aspect ratio 30 Å height:1500 Å length). Similar elongated structures were observed with Ag on Si(100) by Hembree and Venables [2], and, more recently, three dimensional $CoSi_2$ hut clusters were imaged by Scheuch *et al.* [3] for clustering on Si(100) when codepositing thin layers of cobalt and silicon. In all these studies strain is indicated to be the driving factor in creating rectangular clusters. In a recent report Tersoff and Tromp [4] proposed that a strain-induced shape transition may occur from square to rectangular islands, resulting in the spontaneous formation of quantum wires. A tradeoff between surface/interfacial energies and stress relaxation in the three dimensional islands due to elastic distortions of the substrate is suggested as the cause for a substantial elongation of initially square clusters as the cluster volume increases. Experimental data on Au_4Si islands by Sekar *et al.* [5] show the predicted increasing aspect ratio with volume, but a quantitative comparison was not obtained due to the absence of a reduction in island width.

Several problems arise when an attempt is made to study consecutive shape changes of clusters. First, in order to measure a length:width ratio as a function of increasing cluster volume, material must be added continuously. Continuous deposition from a vapor phase or a molecular beam appears inadequate since this not only increases the size of clusters in a very dilute initial cluster morphology, but also causes new clusters to be created. As a result intercluster distances become small, and elongation is interfered with due to cluster interaction. Second, for most growth techniques, *in situ* imaging of cluster growth at elevated temperatures as material is added to the surface causes significant experimental difficulties. Here we report on the growth of $CoSi_2$ clusters on the surface of Si(100) that are much larger than those reported previously [3]. Instead of small 3D clusters forming in large numbers and coalescing, the clusters studied here are much farther apart, and cobalt is continuously fed independently to each cluster from a subsurface reservoir.

The implant stage of a General Ionex 1.7 MV Tandem accelerator is used for cobalt implants at 450 keV into commercially available *n*-doped Si(100) wafers (T_{Si} = 375 °C). This results in a Gaussian implant profile centered around 330 nm depth. The dose (6×10^{16} atoms/cm^2) used in this experiment is not large enough for a continuous buried $CoSi_2$ film to form during the subsequent anneal. Annealing of the implanted Si wafers is done in the controlled environment of a molecular beam epitaxy chamber (base pressure 3×10^{-10} Torr). During the anneal of 60 min at 950 °C the pressure does not exceed 10^{-9} Torr. Rutherford backscattering is used to study the redistribution of cobalt due to the anneal. Compositional studies on the resulting structures on the surface are done with Auger electron spectroscopy. The shape of surface features is analyzed using a Hitachi S-4500 field emission scanning electron microscope (FE-SEM) with a resolution of about 1.5 nm at 30 kV and about 3 nm at 1 kV.

A first consequence of the high temperature anneal is the forming of thermal etching pits (TEP's). These have been observed previously by, for instance, Gómez *et al.* [6] and result from an attempt by the silicon surface to minimize its energy. Their orientation depends on the orientation of the substrate, resulting in rectangular centers along either the (011) or $(0\bar{1}1)$ direction, and it should be noted that there is no preference for either orientation. Although previously presumed to be surface features, these TEP's provide a highly effective diffusion channel back to the surface for implanted cobalt ions.

As observed in Fig. 1(a) the cobalt starts to form a cluster as it reaches the surface. The TEP, responsible for the diffusive link between the cluster and its implanted Co

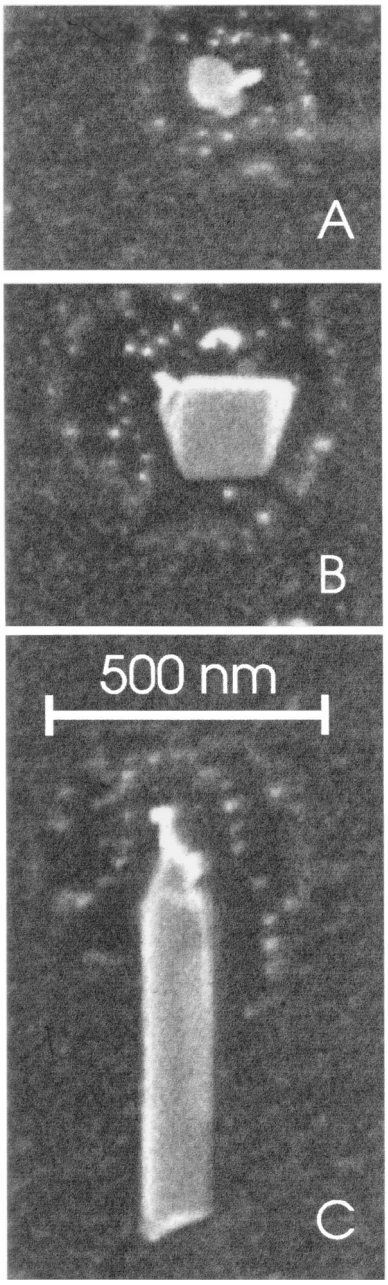

FIG. 1. Three stages of growth are shown as imaged using FE-SEM. In (a) growth is just starting, resulting in an ill defined but fairly symmetric shape. For larger sizes (b) the clusters are square, until a shape transition to rectangular clusters (c) occurs.

source, is already covered at this point. From a comparison between the cluster surface coverage obtained by large area FE-SEM images and an elemental analysis of the surface using Auger spectroscopy, we find that the composition of the clusters corresponds to $CoSi_2$ within 4%. This was, in fact, to be expected considering the high temperature of the anneal since earlier studies showed that the disilicide already starts to form around 600 °C [7,8]. With more cobalt diffusing to the surface the size of the clusters will increase in all directions at first [Fig. 1(b)]. Then, when a certain critical size is reached, it starts to grow outward from the TEP [Fig. 1(c)]. The direction of growth is always one of four crystallographic orientations [(011), $(01\bar{1})$, $(0\bar{1}1)$, or $(0\bar{1}\bar{1})$]. Growth in two directions from the same TEP is never observed. It would correspond to two interconnected clusters which should rapidly coalesce and minimize their shape with respect to their combined volume.

Because the TEP's form throughout the anneal each TEP will start acting as a diffusion channel for the implanted cobalt atoms at a different time. Thus, cobalt diffusion through the TEP's, and subsequent cluster growth, is initiated continuously during the anneal. Consequently, *clusters of all ages* are present on the surface, but with a strong reduction in number with increasing size. This is likely due to a decreasing growth rate as the implanted layer gets depleted during cluster growth. A subtle balance must now be achieved where a sufficient number of long clusters is obtained to observe the elongation, while realizing that a dilute morphology of noninteracting clusters cannot be maintained if too many clusters form on the surface. With an annealing temperature of 950 °C for 60 min we obtained both a large range of cluster sizes (up to 1.5 μm) and an acceptable inter-TEP distance of about 2.5 μm.

A closer study of the cluster sizes shows a strong relation between the clusters width s and length t, as indicated by the dependence of s and t on the surface area A in Fig. 2. Since clusters of all ages are present on the surface and all cluster sizes lie on a single curve, all clusters must, in fact, go through the same stages during their growth. It

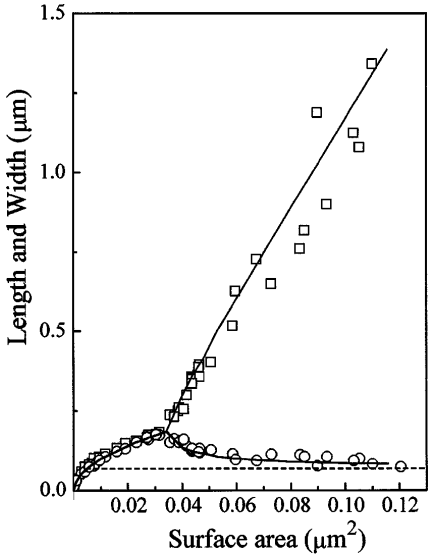

FIG. 2. Dependence of both cluster length t (squares) and width s (circles) on the cluster surface area A. The solid lines represent a theoretical fit obtained with Eq. (1). The initially square clusters ($s = t \sim \sqrt{A}$) undergo a shape transition at $s = t = e\alpha_0 = 185$ nm. Note the predicted reduction of s to close to $\alpha_0 = 68$ nm for large t, indicated by the dashed line.

provides us with the benefit to determine the consecutive stages of cluster growth without actually having to monitor the growth of one single cluster. On the first part of the curve, growth is just beginning, and the shape of the clusters is, in fact, not well defined [Fig. 1(a)], rendering the definitions of s and t somewhat arbitrary. However, in this range the dimensions are nearly identical along s and t, resulting in a square-root dependence of either parameter on A. In fact, the square shape of the cluster becomes better defined as its size increases and the rectangular shape is clearly visible for clusters larger than 80 nm [Fig. 1(b)]. As the cluster area increases further, a transition occurs to a rectangular shape [Fig. 1(c)]. From Fig. 2 it follows that for clusters larger than 185 nm, t starts to increase much more rapidly while s decreases. The decrease of s is a clear indication that we are not simply dealing with a cluster growing outwards from a TEP, but that the cluster is simultaneously trying to minimize its energy.

This observation is in agreement with the model by Tersoff and Tromp [4], who derived an analytical expression for the energy E of a strained epitaxial island. For a cluster of height h, contact angle θ, and volume V they found

$$\frac{E}{V} = 2\Gamma\left(\frac{1}{s} + \frac{1}{t}\right) + \frac{1}{h}(\gamma_i + \gamma_t - \gamma_s) - 2ch\left[\frac{1}{s}\ln\left(\frac{se^{3/2}}{h\cot\theta}\right) + \frac{1}{t}\ln\left(\frac{te^{3/2}}{h\cot\theta}\right)\right], \quad (1)$$

where $\Gamma = \gamma_e \csc\theta - (\gamma_t + \gamma_s - \gamma_i)\cot\theta$ (units $\mathrm{J/m^2}$) and the constant c (units $\mathrm{J/m^3}$) depends on the island bulk stress σ_b, poisson ratio ν, and shear modulus of the substrate μ as $c = \sigma_b^2(1-\nu)/2\pi\mu$. γ_i is the cluster-substrate interfacial energy, and γ_t, γ_s, and γ_e are the surface energies per unit area of the cluster's top, the substrate surface, and the cluster's side facets, respectively. The first two terms give the change in surface and interfacial energies when a cluster forms on the surface in the absence of a wetting layer (Volmer-Weber growth). The third term describes the bulk stress in the cluster due to the substrate-cluster lattice mismatch ($\sim$1.2%). This stress causes the cluster to exert a force on the substrate, resulting in an elastic deformation that lowers the energy of the cluster at the cost of some strain in the substrate. Minimization of the total energy expression for a cluster of constant height h with respect to both s and t yields a square cluster with $s = t = \alpha_0$, where the optimal size α_0 is given by

$$\alpha_0 = e\phi h \exp(\Gamma/ch). \quad (2)$$

As described in Ref. [4], when increasing the cluster volume beyond this optimal size, the optimum shape remains a square up to $s = t = e\alpha_0$. At this critical size $e\alpha_0$ a shape transition occurs, and a further increase of the cluster volume results in a reduction of the width back to the optimal size α_0, while the length increases rapidly (thus $t/s > 1$). Through Eq. (2), an experimental observation of the critical size at which the shape transition occurs determines the relative importance of the first and third terms in Eq. (1) (the ratio Γ/c), while the second term is irrelevant for the minimization when h is constant.

A comparison of this model with our data shows excellent agreement for $e\alpha_0 = 185$ nm, as indicated in Fig. 2. We have used $h = 30$ nm and $\theta = 20°$, but it should be noted that changing the value for h or ϕ only changes the depth of the energy minimum, while the obtained values for t and s remain unchanged. For the longer clusters we indeed observe the expected decrease of s as it approaches the value $\alpha_0 = 68$ nm, indicated by the dashed line in Fig. 2.

This suggests that the theoretical assumptions in the model are adequate. However, it was indicated by Khor and Das Sarma [9] and in Ref. [4] that the validity of the calculations depends critically on the condition that the height is relatively constant. They show that when h is taken as a variable and the energy is minimized with respect to volume, $V = hst$, instead of surface area, $A = st$, one obtains an aspect ratio t/s of *one* for all cluster sizes. In this respect, Tersoff and Tromp [4] indicated that although h may vary slowly compared to s and t, it will inevitably increase and result in a triangular cross section for $h \geq 2\Gamma/c$. For the present study aerial views similar to Fig. 3 suggest no significant changes in h, indicating changes in height may only occur on a significantly longer time scale rendering the model applicable. In order to check the consequences of clusters which adjust their height, we implanted a second sample at a much lower dose (9×10^{15} atoms/cm^2) and increased the annealing time to 2.5 h. In this case growth is limited by the amount of

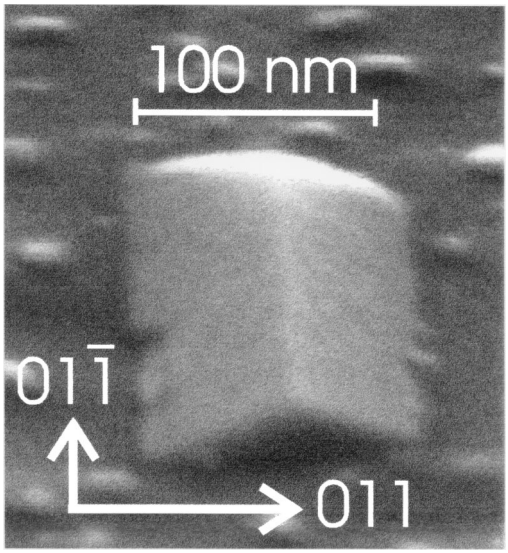

FIG. 3. FE-SEM image of a $CoSi_2$ cluster with a triangular cross section on Si(100). The image is taken at 15° with the in-plane direction along the length of the cluster.

implanted cobalt (instead of the annealing time as before) which, considering the homogeneity of the implant, should result in a narrow distribution of cluster sizes. This is indeed the case with all lengths observed between 200 and 400 nm. Additionally, these clusters have apparently reached their optimum height as indicated by the triangular cross section noted in Fig. 3. This result may, however, not necessarily contradict the calculations in Ref. [9] as the observed clusters could still be reducing their aspect ratio back to unity now that their optimum height has been obtained.

In conclusion, we have presented experimental data confirming theoretical calculations by Tersoff and Tromp [4]. It shows the abrupt transition at the critical size $e\alpha_0$ from square clusters to a regime where the clusters are actively minimizing their energy through a shape transformation. This results in a quick increase in length and a reduction of the cluster width, back to the optimum value α_0. When the cobalt available for each cluster is reduced we observe a narrow size distribution of rectangular clusters with a triangular cross section.

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