Available online at www.sciencedirect.com
ScienceDirect
Surface Science 601 (2007) 2756–2761
SURFACE SCIENCE
www.elsevier.com/locate/susc

In-plane and out-of-plane shape transitions of heteroepitaxially self-assembled nanostructures

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Abstract

In this work, shapes and shape transitions of several types of self-assembled heteroepitaxial nanostructures, as observed in in situ scanning tunneling microscopy experiments during growth, are examined in the framework of several equilibrium and kinetic models. In particular, heteroepitaxial $TiSi_2$ and $CoSi_2$ islands on Si(1 1 1) are shown to behave in accordance with generalized Wulff–Kaishew theorem of equilibrium strained and supported crystal shapes. More specifically, these silicide nanocrystals exhibit *out-of-plane* thickening shape transition by increasing their vertical aspect ratio with growth, as long as they are strained, and inverse (flattening) transition upon relaxation by misfit dislocations. On the other hand, heteroepitaxial Ge and $CoSi_2$ islands on Si(0 0 1) are well-known for their *in-plane* anisotropic elongation. Plausible energetic and kinetic reasons for such elongation, based on the unique nucleation features of Ge–hut/Si(0 0 1) and non-planar $CoSi_2$–hut/Si(0 0 1) interface, are discussed.

Keywords: Vapor-phase epitaxy; Self-assembled nanostructures; Surface structure, morphology, roughness, and topography; Surface thermodynamics; Scanning tunneling microscopy; Germanium; Silicides

1. Introduction

It is important to understand the factors that govern shape and size of nanocrystals, self-assembled on surfaces due to strained-layer heteroepitaxial growth, if they are to be used in realistic devices. Simultaneous discovery of strained, crystallographically-perfect nanometric Ge/Si(0 0 1) [1,2] and $In_{0.5}Ga_{0.5}As$/GaAs(1 0 0) [3] three-dimensional (3D) islands has motivated large body of work, mainly due to their potential as building block in futuristic, low-dimensional, quantum photonic and single-electron devices [4].

In their fundamental work, Tersoff, Tromp, and LeGoues have laid the theoretical foundations for understanding strained-layer (Stranski–Krastanow (S–K) and Volmer–Weber (V–W)) nucleation and growth behaviour of self-assembled nanostructures, by showing that at moderate mismatches elastic relaxation of mismatch strain by substrate distortion (due to force density applied by tilted facets), competes with plastic relaxation by misfit dislocations at lower mismatches, and that in cases where the island height growth is kinetically limited – an island exceeding some critical size becomes unstable against anisotropic elongation [5,6]. Many of the major model's conclusions have been experimentally validated, e.g. dependence of the $Si_{1-x}Ge_x$/Si(0 0 1) island size on the square of strain [7], transition of implanted $CoSi_2$/Si(0 0 1) islands from compact to elongated shape at sizes above critical [8], and the formation of strain-relieving pits in the wetting layer even before the islands are formed [9]. Perhaps surprisingly, elongation of Ge/Si(0 0 1) huts in a kinetically-limited regime does not seem to obey the equilibrium elongation model of Tersoff and Tromp [5]. Even more surprising, elongation of epitaxially grown $CoSi_2$/Si(0 0 1) islands is very different from the $CoSi_2$/Si(0 0 1) islands obtained by ion-implantation by Brongersma et al.

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doi:10.1016/j.susc.2006.12.042

[8]: while the latter seem to beautifully fit the equilibrium elongation model [5], in the sense that there is a critical $e\alpha_0$ size above which the islands keep elongating in one direction and shrinking back to α_0 in the other, the former do not exhibit these features, although their width grows slower than length. By using anisotropic mismatch of hexagonal rare-earth silicides, Chen et al. [10] have intentionally grown nanowires elongated along the lower-mismatch direction, minimizing the more highly strained parts of the island. However, for more symmetrical, cubic crystals, Jesson et al. [11] and Voigtländer [12] proposed kinetic growth instability models (as an alternative to equilibrium elongation of Tersoff and Tromp [5]), based on the barrier to adatom attachment to a facet or on the facial-layer nucleation barrier due to interaction of steps comprising the vicinal facet, respectively.

On the other hand, if there are no limitations to the island's height growth, according to generalized Wulff–Kaishew theorem the most effective relaxation with increasing volume would be achieved by thickening in the vertical direction, i.e., by growing more upwards than sideways, ultimately resulting in high vertical aspect ratios and sharp crests [13]. Such thickening transition can be accomplished by a replacement of shallow facets by steeper ones, as in Ge/Si(001) pyramid–dome transition [14–16], and in a similar transition in the InAs/GaAs system [17]. Sharpening of growing strained $TiSi_2$ and $CoSi_2$ islands on Si(111), followed by reverse (flattening) transition upon strain relaxation by misfit dislocations, shown in this work, is another example.

2. Experimental

The experiments were performed in an ultra-high vacuum (UHV) variable-temperature scanning tunneling microscope (VT–STM), equipped with surface electron diffraction apparata, Auger electron spectrometer, and capable of operation up to 1250 °C by direct-current heating. Si (111) and (100) wafers were chemically degreased and cleaned *ex vacuo*, and introduced into the UHV. In UHV (base pressure 1×10^{-8} Pa), after thorough degassing, the oxide was evaporated by repeated flashes at 1150–1200 °C, and the clean Si surface was left to order during a slow cool to the desired temperature, until well-ordered (111)–(7×7) and (001)–(2×1) surfaces were observed in diffraction and STM images. Ti and Co for silicide nanostructure growth were evaporated from a precise e-beam evaporator onto Si(111) at room temperature (RT) and Si(001) at 500 °C, respectively, mounted at the VT–STM stage, subsequently undergoing a series of annealing treatments in the STM under continuous imaging. Ge was grown on Si(001) from GeH_4 in a 350–480 °C temperature range, under continuous imaging, as well. STM images were acquired using conventional tunneling conditions of $I = 0.1$–0.2 nA and $-3.0\ \text{V} < V < +3.0\ \text{V}$ in a constant-current mode.

3. Results and discussion

3.1. Out-of-plane shape transitions

3.1.1. $TiSi_2$ nanocrystals on Si(111)

Fig. 1 catches the most important evolution stages of the titanium silicide nanocrystals on Si(111) with annealing temperature. Up to 500 °C, the shapes of the initially unreacted titanium and then silicide agglomerates, forming a disordered quasi-continuous layer, were difficult to define. At 500 °C (Fig. 1a), even though the appearance is still quite disordered, coalescence and coarsening processes already created tiny but clearly round-shaped nanocrystals. The effect of raising the temperature by 60 °C was even more profound on the nanocrystal shape, size, and density: as can be seen in Fig. 1b, the significant increase in the mean size was followed by similarly significant decrease in the nanocrystal number density and transformation of the round-shaped particles into cone-like ones. However, the cones became more and more truncated upon further annealing at 600 °C and 660 °C (Fig. 1c–d). Considerable increase in the mean nanocrystal size accompanied by disappearance of the small-sized ones and drastic reduction in number density, obvious in Fig. 1, is a clear signature of Ostwald ripening [18,19].

The observed shape transformations of $TiSi_2$ nanocrystals can be accounted for in the framework of generalized Wulff–Kaishew theorem of equilibrium crystal shapes (ECS). The total free energy of lattice-mismatched (strained) formation of heteroepitaxial $TiSi_2$ island of volume "V" on Si surface in a Volmer–Weber mode, is composed of the change due to formation of a solid from supersaturated dilute phase, formation of new surfaces (facets) and interfaces, and, finally, the elastic energy stored in the island/substrate system [13],

$$\Delta G = -\Delta\mu V + \left\{ \sum_i \gamma_i A_i + A_{\text{int}}(\gamma_{\text{TiSi}_2} - \beta) \right\} + cV\varepsilon^2 R \qquad (1)$$

where $\Delta\mu$ is the chemical potential difference between dilute and compact phase, γ_i and A_i are the surface energy and area of the i-facet, respectively, γ_{TiSi_2} is the energy of the $TiSi_2$ surface parallel to the substrate, A_{int} is the interface area, and β is the Dupré adhesion term. In the last, strain-related term, c contains the relevant island–substrate elastic constants, ε is mismatch-strain, and (fully relaxed) $0 < R < 1$ (fully strained) is the shape-dependent relaxation factor. A Volmer–Weber nanocrystal of fixed volume and n_i facets inclined by θ_i to the substrate's surface assumes its ECS when all the partial derivatives of ΔG go to zero, resulting in an equilibrium vertical aspect ratio:

$$r_i = \frac{2\gamma_{\text{TiSi}_2} - \beta + cV\varepsilon^2 \left.\frac{\partial R}{\partial A_{\text{int}}}\right|_{A_i}}{\gamma_i - \gamma_{\text{TiSi}_2}\cos\theta_i + c\varepsilon^2 \left.\frac{V}{n_i}\frac{\partial R}{\partial A_i}\right|_{A_{\text{int}}}} \qquad (2)$$

Since most of the strain is concentrated at the island/substrate interface region [11,20], extension of the interfacial