Evolution of epitaxial titanium silicide nanocrystals as a function of growth method and annealing treatments

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Abstract

Titanium silicide grows on silicon in a form of discontinuous layers, which is the most serious obstacle to the formation of high-quality epilayers for VLSI applications. At the same time, nanometric dimensions of the epitaxial silicide islands attract interest as quantum nanostructures. However, for this purpose, nanocrystals in a self-assembled array have to be defect-free, and exhibit high shape and size uniformity. In this work titanium silicide was grown on Si(1 1 1) substrates by reactive deposition epitaxy and by solid-phase epitaxy. Since the reaction and phase-formation kinetics depend on the growth method, accordingly different lattice matching and facet energies may result in different morphological shapes of the nanocrystals. Nanocrystals from reaction in a solid-state could be characterized as highly non-uniform in both shape and size, and their evolution due to post-deposition anneals increased that non-uniformity even further. Relaxation of epitaxial mismatch strain by misfit dislocations could be inferred from a gradual reduction of the nanocrystal vertical aspect ratio and development of flat top facets out of the initially sharp conical crests, in accord with generalized Wulf–Kaishew theorem. On the other hand, the silicide nanocrystals formed by reactive deposition exhibited high uniformity and thermal stability. Significant strain relaxation, as could be judged by the nanocrystal flattening, took place only at temperatures in excess of 650 °C, followed by progressive nanocrystal coalescence. It thus could be inferred, that better titanium silicide nanocrystal arrays (in the sense of uniformity and stability) are more easily obtained by reactive deposition epitaxy than by solid-phase epitaxy. While terminal, stable C54-TiSi2 phase, did eventually form in the epilayers in both methods, different evolution pathways were manifested by different respective morphologies and orientations even in this final state.

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1. Introduction

The interest in epitaxial silicides, particularly refractory metal silicides, such as TiSi2, TaSi2, MoSi2, and WSi2, originally stemmed from their good combination of low resistivity, high thermal and chemical stability, and compatibility with processing steps (e.g. self-aligned “salicide”) in very (VLSI) and ultra (ULSI) large scale integration [1–6]. They can be employed as contact and interconnect materials, as well as the source, drain, and gate electrodes in complementary metal-oxide-semiconductor (CMOS) technology. The advantages of epitaxial over polycrystalline silicides could be numerous: regular atomic arrangement at the silicide/silicon interface would improve ohmic and Schottky contacts as well as the adhesion and allow better control of the heterojunction electronic properties, and the absence of grain boundaries would decrease interdiffusion and electromigration-related problems and increase the stability of shallow junctions. Unfortunately, those silicides that can be grown as single crystal epilayers, e.g. NiSi2 or Pd2Si, are not really useful due to either high resistivity and/or low thermal stability. TiSi2, that exhibits superior resistivity (10–20 μΩ cm), could not be grown as a coherent epitaxial deposit, due to a large lattice and symmetry mismatch with Si, even though some limited epitaxy can be more easily achieved on Si(1 1 1) than on the (0 0 1) surface [2–10]. In addition, TiSi2 suffers from having two polymorphs: the stable, low-resistivity C54-TiSi2 phase in a face-centered orthorhombic Fddd structure (a = 8.268 Å, b = 4.798 Å, c = 8.298 Å, ...).
c = 8.553 Å, JCPDS 35-0785), and a metastable C49-TiSi2 with a base-centered orthorhombic C_{mcm} structure (a = 3.562 Å, b = 13.53 Å, c = 3.550 Å, JCPDS 23-964) with four times higher resistivity (60–75 μΩ cm) [3–10]. (It should be stated, that the lattice constant values for these two structures vary considerably in the literature [4,9–11].) Since the latter is interface-stabilized, and hence its stability (and, consequently, the C49 → C54 transformation temperature) is higher the thinner the film, an excessive thermal budget is required to reach the stable, low-resistivity phase [5,6].

The seminal scanning tunneling microscopy (STM) work of Stephenson and Welland has demonstrated the possibility of growing arrays of small TiSi2 crystallite islands on Si(1 1 1) [11] and (00 1) [12] surfaces. Soon after that, an attempt was made to correlate between the Schottky barrier height and the size of these TiSi2 islands [13], or, alternatively, to check their self-assembling potential for quantum dot arrays [7,8] (e.g., single electron tunneling (SET) effects have been, indeed, observed in these silicide nanoislands, even at room temperature (RT) [14]). However, to improve usability of such epitaxial nanoisland arrays, shape and size uniformity is required. In this work, it is shown how stable and highly uniform titanium silicide nanoisland arrays can be grown on Si(1 1 1).

2. Experimental

The experiments were performed in an ultra-high vacuum (UHV) variable-temperature (VT) scanning probe [STM and atomic force (AFM)] microscope, equipped with reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED)/Auger spectrometer, and capable of operation up to 1250°C by direct-current heating. Si(1 1 1) 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°C, and the clean Si surface was left to order during a slow cool to the desired temperature, as measured by infrared pyrometer with ±30°C accuracy. Such treatment has been effective in producing well ordered (1 1 1)-(7 × 7) surfaces, as was indeed verified at this time by LEED, RHEED and STM. Nominally flat (singular) surfaces were used for solid-phase epitaxy (SPE), and vicinal surfaces (~3° miscut) for reactive deposition epitaxy (RDE).

In SPE, the Ti was evaporated from a precise e-beam evaporator onto the Si(1 1 1) substrate mounted at the VT–STM stage and held at RT, and subsequently underwent a series of annealing treatments in the STM to promote the metal–silicon reaction and silicide formation. About two monolayers (ML’s) of Ti were evaporated. The evaporation and anneals, up to 850°C, were conducted under continuous imaging. In RDE, the evaporation was made onto the substrate preheated to 530°C in the VT–STM stage, and the as-grown specimens were then subjected to the annealing cycles, similarly to those done in SPE. In this case, too, most of the steps were continuously STM-monitored in real time.

3. Results

Fig. 1 displays the evolution of titanium silicide on the Si(1 1 1) surface with annealing temperature, where Fig. 1(a)–(c) show the SPE-grown nanocrystals, and Fig. 1(d)–(f) the RDE-grown ones. Immediately as-deposited at RT SPE surface consists of protrusions of unreacted Ti clusters, which cause a disordered appearance of the surface [15]. Upon annealing, these Ti clusters coalesce, and some dispersion in their mean size is created, however up to 500°C not much is happening in terms of shape, which remains spherical [15]. At 560°C, size distribution widens, and the cluster density is so significantly reduced, that unobstructed patches of (7 × 7)-reconstructed Si(1 1 1) surface are now revealed between them [see Fig. 1(a)]. Another interesting feature at this temperature is that the nanocrystals are no longer spherical, but rather conical with a pointy apex. A slope diagram shown in the inset shows quite a uniform intensity distribution (the central, four-fold symmetrical feature seem to be an artifact of the FFT software), indicating absence of well-defined facets. This changes upon a 600°C anneal: while the general trend of size broadening and decreasing number density continues, both parallel (at the top) and oblique facets begin evolving, as evident from the appearance of the intensity maxima in the slope diagram in the inset, corresponding to the facet angles [Fig. 1(b)]. It also stems from the figure, that in addition to these three-dimensional (3D) domes, there is certain population of 2D triangular and hexagonal islands. Finally, at 660°C, even fewer and larger nanocrystals are seen on the surface, with now well-developed wide top plateaus, and about six points in the slope diagram in the inset corresponding to six mature side facets, inclined by about 19–22° to the surface [Fig. 1(c) and inset].

On the other hand, RDE-grown silicide islands show entirely different behavior. Deposition at 530°C resulted in very narrowly distributed hemispherical or lens-shaped nanocrystals [Fig. 1(d)], that remained intact up until 650°C anneal [Fig. 1(e)], where the array was finally destabilized, and the nanocrystals underwent massive flattening accompanied by strong coalescence. This process eventually resulted in the formation of flat platelets with their surfaces parallel to the substrate’s (1 1 1) surface, as shown in Fig. 1(e) and magnified in Fig. 1(f). Similar platelets were observed on the Si(0 0 1) surface by Medeiros-Ribeiro et al., and identified by them as TiSi2–C54(1 1 0) surface [7].

4. Discussion

Generalized Wulf–Kaishev theorem states that (a) a relaxed crystal grows on the substrate in a self-similar, shape-preserving manner, and (b) mismatch strain acts against wetting [16]. In other words, strain in growing epitaxial crystals tends to thicken them by increasing out-of-plane aspect ratio, for example, by steeper facet inclinations and sharper crests, whereas decreasing aspect ratio by progressive nanocrystal truncation and less steep facets is expected upon relaxation, e.g. by misfit dislocations. While, as was already mentioned, large
mismatch between titanium silicide and silicon lattices makes coherent epitaxial growth of the former on the latter difficult, it is not impossible when the silicide crystal is very small, since the elastic strain energy is a function of volume. Epitaxial strain can account for the evolution of the initially hemispherical islands into pointy cones shown in Fig. 1(a), and gradual relaxation by increasing number of misfit dislocations at the interface can account for the opposite trend, namely progressive truncation and flattening shown in Fig. 1(b) and (c). It can be shown that such a process eventually leads to a shape transformation of all the 3D dome-nanocrystals into flat 2D triangles and, finally, hexagons, which are thought to be the equilibrium state of relaxed TiSi$_2$-C54 islands [17].

In RDE-grown silicide (and germanide) layers, it is often the case that the first phase to nucleate is a silicon- (germanium)-rich one (mostly disilicide or digermanide), because accumulation of metal at the growing metal–semiconductor interface is avoided [18,19]. However, due to a very low thickness of the layer in these experiments (no more than a few ML’s), it is most likely that out of the two disilicide polymorphs, the lens-shaped islands belong to the metastable C49 one [5,6,14]. Perhaps the coherent interfaces of these C49 nanocrystals with Si are responsible not only for the thermodynamic stabilization of C49 relative to C54, but for their shape and size stability, as well, at least up to 650 °C. There the coherency is lost and the strain is relaxed by misfit dislocations, as may be concluded from the nanocrystal

Fig. 1. Constant-current STM topographs of (a)–(c) SPE- and (d)–(f) RDE-grown titanium silicide nanocrystals. Topographs (a)–(e) were filtered to emphasize the slopes (the steeper the darker), and (f) is a current-image blowing-up the rectangular platelet from (e). SPE annealing temperature is (a) 560 °C, (b) 600 °C, and (c) 660 °C. (d) As-grown at 530 °C RDE surface, and (e) annealed at 650 °C. Spots in the slope diagrams in the insets correspond to facets inclined to the surface at an angle determined from their angular distance to the central spot (zero inclination).
truncation and flattening evident from Figs. 1(e) and 2. Since the strain-based barrier to attachment to the island edges is no longer there, the islands may coalesce and coarsen. For example, in the center of Fig. 2(a), coalescing flat-topped nanocrystals are shown, and in Fig. 2(b) is shown what seems to be the chains of coalescing nanocrystals turned into long ridges, both eventually producing flat rectangular platelets, whose atomically resolved structure appears blown-up in the respective insets, and in Fig. 1(f). The model explaining that appearance has been proposed by Medeiros-Ribeiro and co-workers [7], who nick-named it “galette”, where the distance between the parallel rows of atoms [as in Fig. 1(f) and in the insets of Fig. 2] is 8.5 Å, matching the C54 lattice constant in the [0 0 1] c-direction, making the row direction [1 1 0], as shown by the arrow in Fig. 1(f). In the layered C54 structure, rows of atoms [perpendicular to the plane of paper in the ball-and-stick model of Fig. 2(c)] at the top (1 1 0) surface consist of alternating pairs of Ti and Si rows. The latter are either higher [top model in Fig. 2(c)] or lower [mid model in Fig. 2(c)] than the Ti pairs by ~0.7 Å. A mixture of these two terminations can produce a height-variation along Si [1 1 0] row pairs, as shown in the bottom model of Fig. 2(c), and hence may account for the slightly higher “fingers” that cross the rows in Fig. 1(f) and inset of Fig. 2(a). It is worth noting that, although some different orientations of TiSi2 nanocrystals were also detected, the prevailing orientation, covering the majority of the Si surface, was indeed (1 1 0).
5. Conclusions

In this work stability, shape and size evolution of titanium silicide on Si(111) were analyzed by in situ scanning tunneling microscopy, as a function of deposition method and annealing treatments. The goal was to learn more about the factors governing the morphology of the grown layers, with the aim of getting a better control in producing flat continuous epilayers, or arrays of discrete nanocrystals with narrow size and shape distribution.

It appears that suitability of solid-phase epitaxy for either is low. In the metastable (low-temperature) state it produces broad size distributions, with the large-size tail continuously growing with temperature, as shown in Fig. 1(a)–(c) and size-distribution plots in Fig. 3(a)–(e). At the as-deposited at RT surface, and during the first anneals, the close proximity of the islands favors a coalescence-type coarsening mechanism, as evident from the log-normal type distribution function [20] in Fig. 3(a). However already at 560°C, beginning of strain relaxation gives rise to a long tail towards larger sizes [Fig. 3(b)] which, together with a drastic reduction of the nanocrystal number density [Fig. 1(a)] is indicative of an Ostwald ripening-type mechanism [21]. This trend, where coarsening by coalescence competes with Ostwald ripening continues with higher-temperature anneals and further relaxation [Figs. 1(b) and (c) and 3(c) and (d)], eventually leading to a bi-modal size distribution at 660°C [Fig. 3(e)], with both modes being quite broad. Ultimately, at even higher-temperature anneals (i.e. above 750°C), the flattening transforms the truncated domes into flat hexagonal plates [17].

On the other hand, reactive deposition epitaxy produces arrays of lens-shape nanocrystals, shown in Fig. 1(d), with good size and shape uniformity, stable up to 650°C [Fig. 1(e) and (f)], as demonstrated in Fig. 3(f)–(j). However, they are interesting not only because of that, but also because of the indications of Coulomb blockade in them [15]. Even though these uniform arrays were destroyed at 650°C, the resulting rectangular C54 platelets, with their (110) surface parallel to the Si(111) substrate, produce a rather uniform epitaxial coverage.

One of the important conclusions from this work is that coherent epitaxial titanium silicide nanocrystals with good size and shape uniformity (probably due to coherently strained interfaces with Si), showing small-size effects, e.g. Coulomb blockade, can be epitaxially grown on silicon, provided the growth temperature does not exceed 650°C. This temperature seems to indicate some sort of a threshold in Ti/Si epitaxial system, with a dramatic effect on both the SPE- and RDE-grown silicide nanocrystals.

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References


