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Self-organizational tendencies of heteroepitaxial transition-metal silicide nanoislands

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ABSTRACT

The aim of this work was to explore self-organizational tendencies of transition-metal silicide nanoislands formed by heteroepitaxial self-assembled processes, such as Co_xSi_y/Si, Ti_xSi_y/Si, Mn_xSi_y/Si, etc, which may exhibit a variety of intermediate phases, polymorphs, and shape transitions, with unique physical properties and size effects. Recent scanning tunneling microscopy observations of self-assembled growth of $CoSi_2$ nanoislands have shown self-organization of nanoislands at the step-bunches of the vicinal Si(1 1 1) surfaces during solid-phase epitaxial growth, namely room-temperature deposition of sub-monolayer Co followed by elevated-temperature annealing treatments. In the current set of experiments, the specific effects of metal coverage, and of structural mismatch of respective silicide with silicon, were investigated by depositing higher coverage of Co and Ti, respectively, prior to the annealing treatments. Higher Co coverage has drastically modified the process, with flat fractal-type two-dimensional islands covering most of the terraces, though tiny dots were still observed at the step-bunches. The outcome of a higher Ti coverage experiment resembled that of a lower Co coverage with the disc-shaped silicide nanodots preferentially occupying the step-bunch sites; however, with a lesser degree of ordering, quite a few dots were found to populate terrace sites. More importantly, no size-selection took place, i.e., no correlation between the dot size and the parent step-bunch height was observed.

1. Introduction

Transition-metal silicides are convenient as a test ground for exploration of structural and symmetry mismatch effects, at the interface with the substrate, on silicide growth morphology and the resulting physical properties. Heterosystems, such as Fe–Si/Si, Cr–Si/Si, Co–Si/Si, Ti–Si/Si, and Mn–Si/Si, exhibit a variety of intermediate phases with varying stoichiometries, structures, and properties, as well as polymorphs at some fixed composition. For example, Fe_3Si in a DO_3 structure is ferromagnetic, ε-FeSi is a simple cubic metal, high-temperature α-$FeSi_2$ is tetragonal and metallic, whereas low-temperature β-$FeSi_2$ is an orthorhombic direct band-gap semiconductor, and metastable γ-$FeSi_2$ in a CaF_2 structure is interface-stabilized in epilayers [1]. Disilicide polymorphs also appear in a Ti–Si system, known as C49-$TiSi_2$ and C54-$TiSi_2$ [2]. Mn_5Si_3 and MnSi are metallic and exhibit magnetic properties, such as a helical spin structure in B20-type MnSi below ~30 K, while $MnSi_{\sim 1.7}$ is a direct band-gap semiconductor [3,4].

Complications arise when moving from the bulk to thin films, since interface-stabilized structures (unstable or metastable in the bulk, such as γ-$FeSi_2$ or C49-$TiSi_2$) may

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appear. Furthermore, complex interplay between surface and interface and strain energies may cause the formation of discrete two-dimensional (2D) or three-dimensional (3D) compact or elongated islands, which, on the one hand prevent growth of flat continuous layers, yet on the other hand open new possibilities of creating novel low-dimensional devices based on quantum nanostructures. For the latter applications, it is desirable to control the size and shape uniformity of such nanostructures, as well as their positioning on the surface. One of the ways to affect the location of the growing islands is to cause them to "decorate" surface irregularities and domain walls. The easiest way to introduce periodic domain walls is to use vicinal surfaces where a miscut angle sets the periodicity of the step-bunches. Recent experiments have shown that such a decoration can be successfully achieved in $CoSi_2$ [5], $MnSi_2$ [6], and $FeSi_2$ [1] nanoislands. Moreover, by carefully controlling the growth method and parameters, not only the preferential occupation of the step-bunches by nanoislands is possible but also the bunch heights can be used as selectors of the nanoisland sizes [7]. Solid-phase epitaxial (SPE) $CoSi_2$ nanoislands residing at the step-bunches grow at the expense of those located at the terrace sites, until the latter disappear and the former span the entire bunch height. At this point, the ripening process stops, yielding only uniform-sized nanoislands at the step-bunches (terraces unpopulated). In fact, the self-organization has been three-fold: (i) preferential occupation of the step-bunch sites by the nanoislands with almost none residing at the terrace sites, (ii) nanoisland size-selection determined by the parent step-bunch height, and (iii) establishment of some mean periodicity of the nanoislands along their parent step-bunch [7]. An apparent correlation has been found between items (ii) and (iii), to a degree, where at locations with mean terrace width roughly equal the mean nanoisland–nanoisland separation periodicity along the bunch, kind of 2D-ordered patterns have been detected as shown in Fig. 1. Reactive deposition epitaxy (RDE) of Co on an identical vicinal Si(111) surface did not yield the same degree of ordering [8].

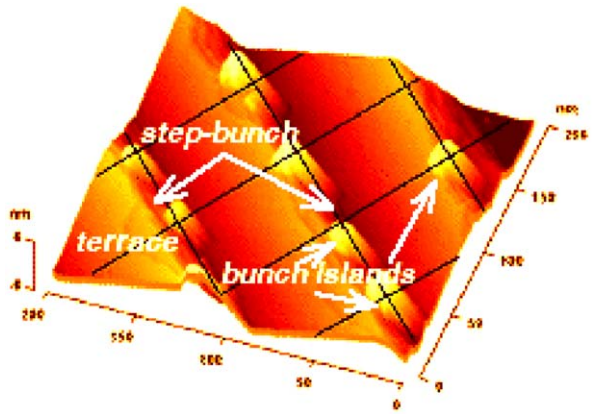

Fig. 1. $200 \times 200 \times 6$ nm 3D representation of a constant-current STM micrograph acquired from a low-coverage Co/vic Si(111) surface after high-temperature anneal in a previous work Ref. [7], demonstrating the degree of self-organization and size-selection.

Mean terrace width and step-bunch height at vicinal Si substrates can be controlled in a rather straightforward manner by an appropriate choice of a miscut angle and by controlling the Si flash parameters, such as the magnitude and direction of the flash current with respect to azimuthal step orientation [9,10]. Hence, such self-ordered nanoisland arrays can, in principle, be obtained in other heterosystems, provided the governing factors are understood. While item (i) above, i.e., preferential decoration of the step-bunches, can be easily interpreted in the framework of a simple terrace–ledge (step)–kink (TLK or TSK) model [11], items (ii) and (iii) are not yet understood. For example, correlation between the nanoisland size and its parent step-bunch height can be equally well accounted for by "uphill climb" [7] or "downhill migration" models [12,13], whereas nanoisland–nanoisland interactions along the step-bunch ledges by mechanical [14] or electronic [15,16] repulsions.

The present set of experiments, namely SPE of similar coverages of Co/Si(111) (i.e., low-lattice mismatch) and Ti/Si(001) (i.e., high-lattice mismatch), was designed to single out the mechanical effects on the one hand, and the effect of coverage, on the other. The results below indicate that (a) coverage is an important parameter in a $CoSi_2$/vic-Si(111) system, where self-ordered nanoislands at the step-bunches (under low Co coverage conditions) were now (i.e., at higher Co coverage) replaced by flat and fractal 2D terrace-islands, but (b) not in a $TiSi_2$/vic-Si(111) system, with truncated 3D nanoislands formed regardless of similar (to Co) coverage variations. This can be attributed to the difference between Co and Ti diffusion mechanisms on Si(111), attachment–detachment kinetics, Co–Si and Ti–Si reaction and silicide island nucleation pathways, and the mismatch of their respective silicides with Si.

2. Experimental

The experiments were performed in an ultra-high vacuum (UHV) variable-temperature scanning tunneling microscope (VT-STM), equipped with low-(LEED) and reflection high- (RHEED) energy electron diffraction, Auger electron spectrometer (AES), and capable of operation up to 1250 °C by direct-current heating. 4°-miscut Si (111) wafers were cut into 10 mm × 1 mm stripes, 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 slowly cooled until well-ordered (111)-(7 × 7) appeared in diffraction and STM images, as shown in Fig. 2(a). Ti and Co, in the respective silicide growth experiments, were evaporated at room temperature (RT) onto Si(111) samples mounted at the VT-STM stage (with time-controlled coverages, calibrated by RHEED, LEED, and STM), and subsequently underwent a series of annealing treatments in the STM under continuous imaging. STM images were acquired using common