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Self-organized trench–island structures in epitaxial cobalt silicide growth on Si(111)

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ABSTRACT

Sub-monolayer Co deposition on clean Si(111)–(7 × 7) surfaces has been found to form nanoscale $CoSi_2$ islands with a surrounding trench of one Si bilayer depth and mainly hexagonal shape. The trench surface structure is largely like that of the disordered '1 × 1' phase of the Si(111)-7 × 7 ↔ '1 × 1' phase transition and comprises mostly disordered Si adatoms with small ordered patches of (11 × 11), (9 × 9), c(5 × √5), c(4 × 4) and (2 × 2) structures along with some Co-ring clusters. This disordered '1 × 1' structure within the trench has formed at 600 °C, the growth temperature of $CoSi_2$ in reactive deposition epitaxy, much below the order–disorder phase transition temperature on Si(111)–(7 × 7). The structure around the trench remains (7 × 7). Electronically the trench is semiconducting. The surrounding 7 × 7 structure being metallic, the island–trench structure forms a lateral metal–semiconductor–metal structure.

1. Introduction

Growth of metal silicides on single crystal Si surfaces has been extensively studied for their importance in fundamental surface science research and possible applications in nanoelectronic devices [1–4]. Metal silicides are an integral part of microelectronics. Their usefulness comes from the chemically and structurally robust silicide/silicon interfaces and the tunability of the Schottky barrier height via choice of the silicide material [5,6]. For nanoelectronics it is important to understand the silicide/silicon systems in the nanoscale. Cobalt disilicide ($CoSi_2$) growth on silicon is important due to its thermal stability (up to ~900 °C) and its application as infrared detector [7,8], high speed transistor [9], low resistivity interconnect and contact material in sub-hundred nanometer device fabrication [10,11]. Growth of epitaxial and endotaxial self-organized cobalt silicide nanostructures on Si substrates of various crystallographic orientations is of tremendous current interest [12,13] and new phenomena in self-organized growth are still being discovered [13]. Here, we report on the epitaxial growth of self-organized $CoSi_2$ nanoislands on Si(111), which occurs via a trench formation around the islands. Although some trench–island structures were earlier observed for manganese silicide [14,15], cesium silicide [16] and iron silicide [17] growth on Si, no details of these structures have been investigated. Here, we present a detailed study of the trench–island structure regarding the trench-shape, relative trench edge energies, relation between trench volume and island volume, and geometrical and electronic structure within as well as outside the trench.

Trenches or vacancy islands on surfaces have been used to study many different kinds of phenomena. Vacancy island formation on various metal (Ag, Pt, Cr, Cu) surfaces has been extensively investigated [18–24]. Vacancy islands have been obtained via many different processes. Simultaneous growth of Ag adatom island and vacancy island on Ag(111) by modification of substrate surface using a vibrating scanning tunneling microscope tip has been investigated by Freund et al. [18]. The structure of the trench edges has been related to step formation energy. Vacancy islands have been formed via etching or sublimation of Cr atoms from a Cr(001) surface [19]. In this work the authors have investigated the morphological evolution of the surface as the atoms are removed. On the Pt(111) surfaces, vacancy islands have been formed by ion sputtering [20]. These authors have investigated the equilibrium shape of the trenches and determined the relative step free energies of different types of steps determining the trench morphology. Monatomic layer deep vacancy formation was observed on Cu(111) surfaces by depositing submonolayer quantities of Co [21,22], Fe [23] and Cr [24]. Quantum states of a two dimensional electron gas confined in a monolayer deep hexagonal trench have been investigated in Ref. [21]. Although most of the investigations on trench are on metal surfaces, there are some cases involving semiconductors (Si). Trenches (voids) were created in Si by He ion implantation followed by thermal annealing in order to investigate equilibrium crystal shape [25]. On a Si(111)-7 × 7 surface bilayer deep trenches were fabricated using a scanning tunneling microscope [26]. For silicide growth on Si, formation of trenches of irregular shapes has been observed for manganese silicide, cesium silicide and iron silicide growth [14–17]. We observe trench formation on Si(111)-7 × 7 surfaces and

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concomitant growth of $CoSi_2$ islands inside the trench upon cobalt deposition at 600 °C. In earlier cases of silicide growth on Si, where trench–island structures were observed, no details of these structures were investigated. We have investigated several interesting aspects of trench–island structures. The trenches have predominant shapes guided by the substrate symmetry. Trench on the Si surface is created due to loss of Si atoms from the topmost bilayer of the Si(111) surface. These Si atoms have been consumed in the growth of $CoSi_2$ islands around which the trench is formed. Beyond the trench the Si(111) surface remains (7 × 7) reconstructed, like the original Si(111)-7 × 7 surface before Co deposition. The exposed surface within the trench is composed mostly of disordered Si adatoms along with small patches of ordered Si(111)-(9 × 9), -(11 × 11), -c(5 × √5), -c(4 × 4) and -(2 × 2) structures. Interestingly, these features are similar to the disordered high temperature '1 × 1' phase of the 7 × 7 ↔ '1 × 1' phase transition on the Si(111)-7 × 7 surfaces [27]. The trench also appears to have some cobalt-reacted ring clusters [28,29]. We also compare the electronic structure within the trench and on the $CoSi_2$ islands.

2. Experimental

Clean Si(111)-(7 × 7) surfaces were prepared from phosphorus doped (10–20 Ω-cm), oriented (within 0° ± 0.5°) Si(111) wafers. The substrate was degassed by heating it for 12–14 h at ~700 °C and then flashing at ~1250 °C for 1 min under ultrahigh vacuum (UHV) condition. This process produces a clean Si(111)-7×7 surface. The base pressure in the UHV chamber was 5×10^{-10} mbar. Epitaxial $CoSi_2$ nanostructures were grown on the atomically clean Si(111)–(7 × 7) surface by depositing 0.5 monolayer (ML) cobalt from a Knudsen cell onto the heated (600 °C) silicon substrate. Here, one monolayer of Co is equivalent to the atomic density on an ideal Si(111) surface (7.84×10^{14} atoms/cm^2). The Co deposition rate was 0.38 ML/min. The deposited amount of Co was determined in situ with a quartz crystal microbalance thickness monitor. A 1.5 Amp direct current was passed through the substrate for 15 min before Co deposition to achieve the substrate temperature. The substrate was maintained at the same temperature for another 10 min following Co deposition. Then the sample was allowed to cool down to room temperature (RT) before scanning tunneling microscopy (STM) measurements were made. The sample was transferred in situ from the growth chamber to the STM chamber (3×10^{-10} mbar). All the images were recorded with a scanning tunneling microscope (Omicron Nanotechnology) in situ at RT in the constant current mode.

3. Results

3.1. The trench–island structure

When Co is deposited on atomically clean heated Si(111)-7 × 7 surface or on Si surfaces with other orientations at 600 °C, $CoSi_2$ is formed [30]. While epitaxial $CoSi_2$ islands grow endotaxially (into the substrate) on Si(100) and Si(110) surfaces, on Si(111) surfaces they grow on top of the flat surface [13,31,32]. The islands are predominantly triangular because of the threefold symmetry of the Si(111) surface. The islands which grow near the surface step edges do not create trenches around them, as seen in Fig. 1. This feature was also observed earlier for manganese silicide [15] and in our earlier investigation on cobalt silicide [32] growth on Si(111). The step edges apparently act as the source of required Si for silicide island growth. This type of islands without a surrounding trench is abundant. Additionally, we find that $CoSi_2$ islands away from the step edges grow with a trench around them, although their number is small. Such $CoSi_2$ islands with a surrounding trench are shown in Fig. 2. In Ref. [15], for manganese silicide growth on Si, it was also observed that islands, which grow on a flat terrace away from surface steps, tend to have a trench around them. However in that work, unlike our case, the shape of the trenches was irregular. In the present case, as no trenches were present on the

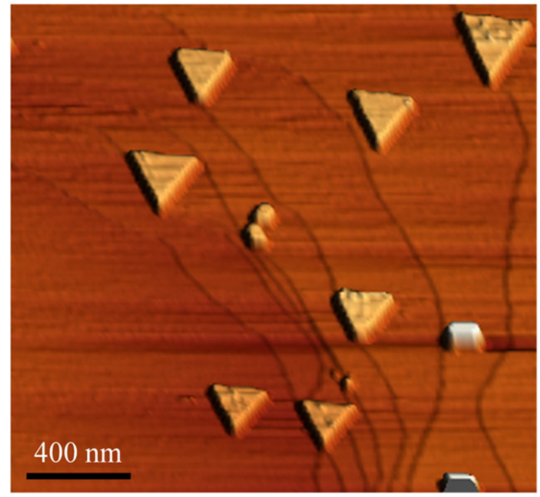

Fig. 1. Three dimensional view of a STM image (sample bias, $V_g = -1.9$ V, tunneling current, $I_t = 0.1$ nA) showing cobalt disilicide islands near the step edges on a Si(111) surface.

clean Si(111)-7 × 7 surface before Co deposition, it is clear that these trenches grow during silicide island formation. These trenches are typically 400–500 nm wide and 0.31 nm deep [equivalent to (111) planar spacing or removal of one bilayer Si]. The missing Si atoms from this trench region are apparently consumed in the growth of the $CoSi_2$ island inside the trench. Fig. 2(a), (b) and (c) shows STM images of island growth with a surrounding trench with three different island–trench structures. Islands are triangular and/or truncated triangular in shape whereas the trenches are hexagonal or partially rounded hexagonal shaped. The truncated $CoSi_2$ triangular island edges are parallel to the edges of the hexagonal trench. [In Fig. 2(c), we notice two intruding islands from the left side into the trench. There is an atomic step (not seen in the figure) present on the left side at ~320 nm from the left edge of the trench. So the intruding islands are a part of step–island structures like those in Fig. 1.]

Let us now discuss the shapes of islands and trenches. There are several theoretical studies on the shapes of islands and vacancy islands (or only trenches) on substrates of threefold symmetry [33,34]. The Si(111) surface possesses threefold symmetry. The growing $CoSi_2$ islands follow the substrate symmetry. So the formation of equilateral triangle shaped islands is quite natural. By Kinetic Monte Carlo simulation, Michely et al. [33] and Liu et al. [34] have found formation of different shapes of islands, including triangular and hexagonal on a surface of threefold symmetry. As shown and clarified in Ref. [33,34], the hexagonal islands on fcc(111) surfaces have two types of edges. The competition of advancement rate of these two types of edges would finally determine the shape of the island. When one type of edge advances faster than the other one, we are left with triangular hexagon shape. In the opposite case, we get an inverted triangular hexagon. If both edges compete equally the island attains an equilateral hexagon shape. The substrate symmetry serves to dictate not only the island shape but also the shape of the trench during the substrate etching. These shapes are seen in our island–trench combined structures. The shape of two-dimensional trenches or vacancy islands has also been investigated on a surface of threefold symmetry [Pt(111) surface] [20]. Experimentally the authors in Ref. [20] have found hexagonal shapes with unequal lengths of adjacent sides, similar to that in Fig. 2(c). Theoretically they have found that with increasing temperature the edges become rounded. However, in experiment, even at a given temperature, they have observed variations in shape [20,33,35], many of those are like the shapes in Fig. 2(a), (b) and (c). Although this kind of trench shapes has been observed on metal (111) surfaces, to our knowledge, there is no report on their observation on Si(111) surfaces.