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Endoepitaxial growth of *hexagonal*-$Fe_{13}Ge_8$ islands on Cubic-Ge(001)

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ABSTRACT

The growth and shape evolution of epitaxial $Fe_{13}Ge_8$ (hexagonal lattice) islands on single crystal Ge(001) (cubic lattice) substrate was observed in real time using an in situ ultra-high vacuum transmission electron microscope (TEM). Post-deposition high-resolution TEM in conjunction with stereographic projection enabled the identification of the interface structure between the $Fe_{13}Ge_8$ islands and the Ge substrate. Only one low-energy coherent interface formed via $Fe_{13}Ge_8$ islands growing into the substrate along the inclined Ge($1\bar{1}1$) plane. This indicates that minimization of net interfacial energy is the driving force for *hexagonal* $Fe_{13}Ge_8$ islands formation on Ge(001).

1. Introduction

Self-assembled epitaxial nanostructures are important for the manufacture of nanoscale electronic devices as shown by extensive studies on a variety of heteroepitaxial systems [1–3]. These nanoscale structures, with remarkable uniformity in size distribution, are of intense interest in science and engineering. Self-assembly provides a potentially low-cost fabrication route to engineer defect-free nanosize structures, which possess fascinating electronic, magnetic, and optical properties that are important for future nanotechnology applications [4–9]. These nanostructures are the integral build blocks in the bottom up processes to nanotechnology [10]. In order to control nanostrutures shape and spatial distribution (*i.e.* for self-organization), it is necessary to develop a detailed understanding of the mechanism for heteroepitaxial nanostructures growth [11–14].

The morphological evolution of metal–semiconductor heteroepitaxial structures is determined through the complex interplay between epilayer/substrate surface energy, interface energy, and strain energy. Heteroepitaxial growth involves the growth of dissimilar materials with different lattice parameters, one atop another. The crystal structure of the deposited layer can have either similar homoepitaxic (e.g., cubic on cubic) or different heteroepitaxic (e.g., hexagonal on cubic) crystallographic systems. The accepted explanation for island shape evolution, during heteroepitaxial growth of isotropically strained islands with similar crystal structure, is via strain-induced instability [11,15–17]. Tersoff and Tromp have developed a general approach, based on competition between surface and strain energy [11]. This model predicts that each island has a critical size, beyond which shape transitions occur. Below this critical size, islands adopt an isotropic shape (*i.e.* a square shape for cubic systems). Continual growth beyond this critical size, results in a decrease in width with a corresponding increase in length, thereby forming a wire. Extensive experimental observations of cubic-$CoSi_2$ on Si(001), Cu_2O on Cu(100) and $TiSi_2$ on Si(111) systems [18–20] can be elucidated by using the Tersoff and Tromp model. In addition, other authors report wires in anisotropically strained systems [12,21,22]. In order to account for the shape evolution in such systems, Pradhan et al. [14] developed a general approach to island shape evolution dealing with both isotropically and anisotropically strained islands. Their model predicts that there is no shape instability as the nucleated islands are anisotropic in morphology. The treatment by both of these models, to the first order, provides elegant means of understanding shape evolution in real materials. However, the lack of interfacial energy, which, by itself, can lead to these shape transitions, renders their models incomplete. He et al. [13] also put forth a mechanism for wire growth not dominated by strain. The mechanism involved epitaxial growth into the substrate, originally termed 'endoepitaxy' by Fathauer et al. [23]. They demonstrated that wire formation of cubic-$CoSi_2$ on Si substrates occurs by endotaxy rather than by, the previously assumed, strain-induced shape transition. All these previously mentioned models, based purely on energetic considerations, contradict the experimental observations of wire formation [11,18–20].

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For island evolution of heteroepitaxial systems with different crystal structures, the growth factors and conditions that could affect or control island formation, due to reduction in symmetry, are more complex and are still not well understood. A previous study has shown the dynamics, formation, and selective growth of low-dimensional epitaxial $Fe_{13}Ge_8$ structures (zero-dimensional (0D) compact islands or one-dimensional (1D) wires of different aspect ratios) in *real time* [24]. Both types of island (0D/1D) share the same epitaxial relation with the underlying Ge substrate [24]. This work demonstrated that *hex*agonal $Fe_{13}Ge_8$/Ge(001) islands grew into wires due to kinetic growth constraints in terms of anisotropy caused by ledge diffusion and corner barriers, rather than purely through the widely accepted equilibrium shape transition process during growth [12,18,19,22,25]. A combination of in situ ultra-high vacuum transmission electron microscopy (UHV-TEM) and post-deposition high resolution TEM (HRTEM) determined the surface and interface structure of *hex*agonal $Fe_{13}Ge_8$ on a Ge(001) substrate.

2. Experimental

A JEOL JEM 2000V in situ UHV-TEM (base pressure of 1×10^{-9} Torr) equipped with an electron beam evaporator (Fe rod, 99.95%), sample heating capability (room temperature to 1200 °C), a Gatan Image Filter (GIF2000), and a Gatan Dual-Vision (DV300) digital camera [26] enabled both static and dynamic recording of growth. The substrates are 2.5×2.5 mm^2 Ge(001) slabs that were mechanically polished, dimpled, and thinned by Ar^+ ion bombardment from the backside to obtain an electron transparent thin area. Cleaning of this Ge specimen was in deionized water followed by mounting on top of a 6.5×2 mm^2 Si(001) heater plate (p-type, resistivity 6–9 Ω cm). Sample degassing performed at 400 °C for about 2 h followed by flashing at about 650 °C removed native oxide, prior to reactive deposition at the desired temperature. The total deposition time for all samples was 4 h at a constant Fe flux. The Gatan DV300 digital camera captured real time images and diffraction patterns during epitaxial island growth.

A 300 kV Philips CM300 field emission gun TEM performed cross-sectional HRTEM imaging. Preparation of cross-sectional TEM specimens was done by gluing two Fe-deposited slabs, film-to-film, and then vertical sections cut, which were thinned to ~20 μm by mechanical grinding. Final thinning to electron transparency occurred by Ar^+ ion milling in a liquid-N_2-cooled stage with the incident beam angle and energy progressively reduced from 10° to 8° and 5 to 1.5 KeV respectively in order to obtain samples with relatively even thicknesses.

3. Results and discussion

The bright-field (BF) TEM image of single crystal Ge(001) substrate prior to deposition (not shown) is clean without any observable contaminations. After opening the shutter of the electron beam evaporator, nucleation of spatially random islands on the Ge(001) surface occurred. Fig. 1 shows typical BF TEM images during reactive deposition growth at a constant Fe coverage for different deposition temperatures. In these TEM images, nucleated islands appear darker due to diffraction contrast while the underlying Ge(001) substrate appears brighter. Fig. 1 shows the time sequence of TEM images of islands grown at 350 (a), 430 (b) and 480 °C (c), respectively. The three images in Fig. 1a were acquired at times $t=30$, 120, and 220 min. During the growth process, all the islands retained their compact shape, with a mean aspect ratio of ~1 to 1.5. An increase in the deposition temperature to 430 °C (on a different sample, Fig. 1b) shows the formation of islands with two types of morphology, namely, compact and wire-like. All these islands have a mean aspect ratio of ~2.5, which is larger than islands grown at 350 °C (Fig. 1a). With a further increase in deposition temperature to 480 °C (again using a different sample), only elongated islands (wires with aspect

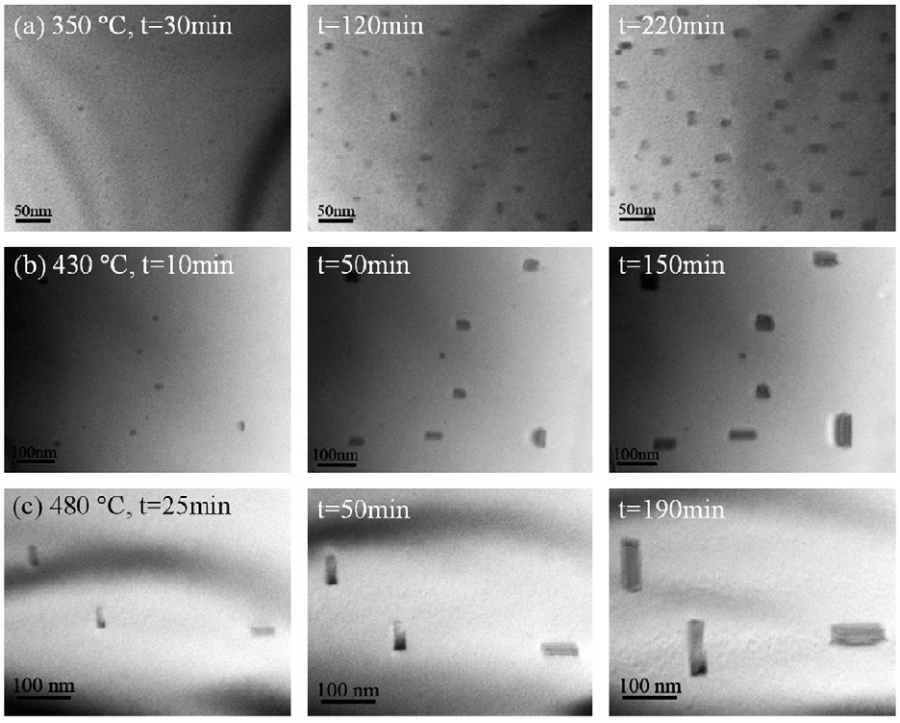

Fig. 1. Shape evolution of growing islands on Ge(001) substrate at different deposition temperatures: (a) 350 °C, (b) 430 °C and (c) 480 °C, respectively.