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Ge islanding growth on nitridized Si and the effect of Sb surfactant

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Abstract
The growth modes of Ge islands on SiN_x-covered Si with and without a surfactant Sb layer are studied by scanning tunnelling microscopy. It is observed that on SiN_x/Si(111), Sb cannot enhance the coverage of (111) facets of Ge islands, which are the dominant features in the late stage of Ge overlayer growth when Sb is not used. However, on SiN_x/Si(001), Sb favours the growth of Ge(001) facets, which will shrink during the islanding growth if Sb is not used. The different behaviours with the (111) and (001) substrates suggest that the surfactant effect of Sb on the islanding growth of Ge on SiN_x/Si is strongly orientation dependent.

1. Introduction

Silicon nitride has been considered a candidate dielectric material for microelectronics applications in recent years. Compared to SiO_2 it is more reliable in a high electric field and under high-temperature operation, and more effective as the diffusion barrier to impurities in device processing. Studies of the growth of semiconductor overlayers on insulating films have attracted wide attention because of their scientific and technological importance. For example, semiconductor–insulator–semiconductor structures are involved in many novel devices. High-quality crystalline GaN film has been grown recently on a silicon nitride film formed on a Si(111) substrate, raising the prospect of integrating GaN optoelectronic devices with Si microelectronic chips [1]. From the viewpoint of applications, a flat and continuous film of overlayer is strongly desired. The growth of a smooth Si or Ge crystalline overlayer on a dielectric film could lead to the realization of novel Si-on-insulator (SOI) structures and also multilayer integrated circuits [2]. In many cases, however, three-dimensional (3D) islanding occurs during the growth of Si or Ge on silicon nitride films [3]. On the other hand, the 3D

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islanding growth provides a unique method for making self-assembled Si and Ge quantum dots on Si substrates. It is well known that with a monolayer surfactant species such as Sb or As deposited on the substrate before epitaxy, the island formation can be suppressed [4–8]. Such surfactant-mediated growth is currently used to improve the quality of strained Si/Ge superlattices [9, 10]. In most previous reports, surfactant effects in the homo-epitaxial growth of Ge or Si and in the Stranski–Krastanov growth of Ge on Si have been investigated. To our knowledge, there are few reports in which the surfactant is used to modify the morphology of a film consisting of faceted 3D islands of different orientations, where a surfactant modifying the surface energy anisotropy could strongly affect the competing growth of islands and facets with different orientations.

In this work we investigate the surfactant-mediated growth of Ge on the surfaces of SiN_x-covered Si(111) and Si(001) substrates. The role of Sb as the surfactant in modifying the growth of Ge overlayers on SiN_x/Si has been revealed. The growth modes of Ge islands on Si(111) and Si(001) under the influence of Sb show strong orientation dependence. Knowledge of the role of Sb surfactant in the Ge island formation might provide useful information as regards controlling the geometry of self-assembled Ge quantum dots.

2. Experiment

The experiments were carried out in an ultrahigh-vacuum (UHV) scanning tunnelling microscopy (STM) system (Omicron, GmbH), which consists of a main chamber and a sample preparation chamber separated by a gate valve. The main chamber with a base pressure $<1 \times 10^{-8}$ Pa is equipped with an STM system and four-grid optics for Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). Both chambers are equipped with electron bombardment heaters for sample annealing. The temperature of the sample was measured by an infrared pyrometer during the annealing. In the main chamber, Si(111) and Si(001) samples cut from commercial wafers and mounted on the sample holder were degassed at 600 °C for a whole night, then annealed at 850 °C for 15 min, and finally heated at 1250 °C for 1 min. After this procedure, clean and flat Si(111)-(7 × 7) and Si(001)-(2 × 1) surfaces were obtained as confirmed by AES, LEED, and STM.

The nitridation of Si surfaces and *in situ* LEED, AES, STM, and *ex situ* cross-sectional transmission electron microscopy (XTEM) analyses of the SiN_x films have been described in detail in previous reports [3, 11–13]. Briefly, clean Si(111) and Si(001) samples were transferred to the sample preparation chamber and then exposed to NO at a substrate temperature of 950 °C for 20 min. During nitridation, the ion gauge in the sample preparation chamber indicated a reading of the pressure of around 5×10^{-6} Pa. The real pressure on the top of the sample surface could be one or two orders of magnitude higher than the reading. The ratio of the Auger peak height at 84 eV for the nitridized Si to that at 91 eV for the elemental Si was used as a rough estimate of the nitride film thickness. The AES measurements showed the presence of nitrogen saturation for both SiN_x films after NO exposure for 20 min.

Germanium and Sb depositions on SiN_x films were performed in the main chamber using two Ta-boat evaporators. The Ge was evaporated initially on the surfaces at a sample temperature of 450–600 °C and a deposition rate of approximately 1 nm min^{-1}. Since the Ge layers grown on SiN_x films are not flat but rough, the values of the Ge film thickness given in our report denote effective thicknesses. Then the sample was annealed at a temperature of 550 °C under the Sb flux to form a maximum coverage of one Sb monolayer (ML) (1 ML = 7.8×10^{14} atoms cm^{-2}). It is impossible to adsorb more than 1 ML of Sb because any excess Sb desorbs immediately at the growth temperature [14]. More Ge was evaporated onto the Sb-covered sample surface afterwards.

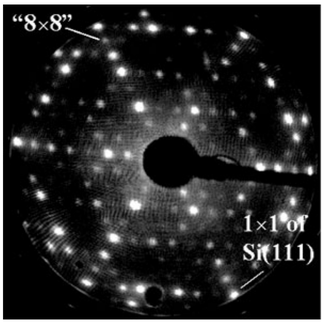

Figure 1. A LEED pattern observed for a silicon nitride film grown on Si(111) at 950 °C. The representative spots for Si(111)-(1 × 1) and '8 × 8' periodicities are marked.

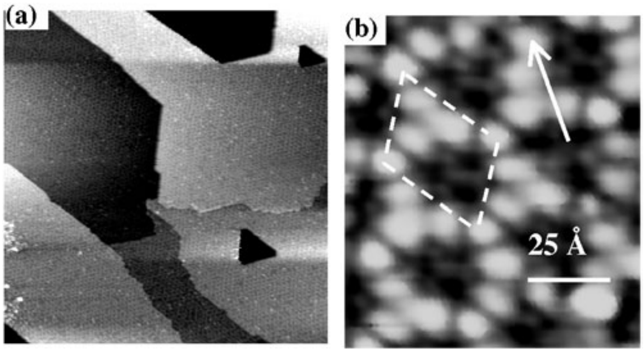

Figure 2. (a) A large-scale STM image of SiN_x film grown on Si(111) at 950 °C. Scanning area: 200 × 200 nm^2. (b) An atomic resolution STM image of a SiN_x film surface.

STM observations were performed at room temperature in the constant-current mode under conditions with the sample bias between −3.8 and +3.3 V and the tunnelling current between 0.2 and 1.0 nA.

3. Results and discussion

3.1. Ge growth on SiN_x/Si(111)

Before depositing Ge, the surface of crystalline SiN_x film formed on Si(111) shows an '8 × 8' LEED pattern, as seen in figure 1. Figure 2(a) displays a large-scale STM image in which terraces and steps characterizing a crystalline film are clearly seen. The atomic resolution image in figure 2(b) indicates the existence of a reconstruction with a periodicity of 0.384 nm × 8 = 3.07 nm on the surface of the SiN_x film. The unit cell outlined with a dashed diamond is suggested to be a (4 × 4) reconstruction on β-Si_3N_4(0001) [11–13]. The orientation of the unit cell with respect to the Si(111) substrate is unique: the long diagonal of the cell is along the direction $[11\bar{2}]$ of the underlying Si(111), as shown by the arrow in figure 2(b). The thickness of the crystalline silicon nitride film is about 1–1.5 nm as measured by high-resolution XTEM.

Deposition of Ge on SiN_x leads to the formation of Ge islands. Figure 3(a) shows a STM image after 15 nm Ge was deposited on SiN_x/Si(111). It seems that the surface free energy of

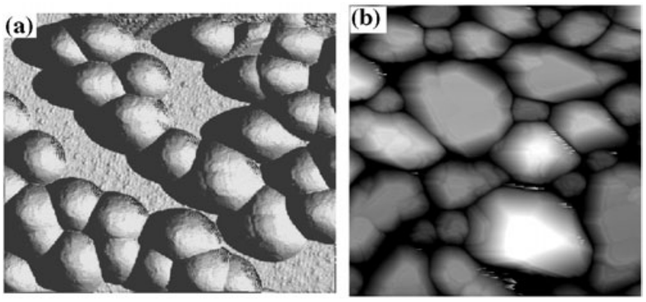

Figure 3. STM images of (a) 15 nm Ge and (b) 200 nm Ge deposited on SiN_x/Si(111). Scanning area: 200×160 nm^2.

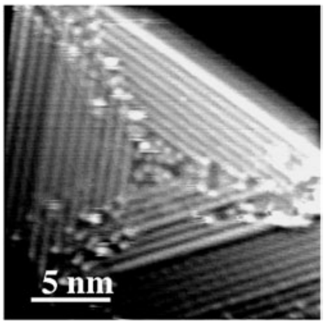

Figure 4. A triangular Ge(111)-(2×1)–Sb top facet formed by three domains.

Ge is larger than that of the crystalline SiN_x film, and the interface energy is relatively high. Therefore, the Ge overlayer grows in a 3D islanding (Volmer–Weber) mode on SiN_x film. These islands are usually spherical in shape with various sizes. The base dimension and height of the islands are 25–40 nm and 10–15 nm, respectively. As more Ge is deposited on the SiN_x film surface, the islands grow bigger and the facets are clearly observed. The morphology of the islands after depositing 200 nm Ge is shown in figure 3(b), where crystalline facets, especially the top facets, are clearly seen. The top facets of the islands are Ge(111)-c(2×8), and the side walls are high-index facets such as {113}. Analysis of the atomic scale STM images obtained on the island facets shows that, at this stage, the orientations of most islands are aligned with the underlying Si_3N_4(0001) and Si(111) substrates, i.e., $(111)_{Ge} \parallel (111)_{Si}$ and $[1\bar{1}0]_{Ge} \parallel [1\bar{1}0]_{Si}$. It is also observed that a small proportion of the islands are rotated by 30° from the aligned orientation, i.e., $(111)_{Ge} \parallel (111)_{Si}$ and $[\bar{2}11]_{Ge} \parallel [1\bar{1}0]_{Si}$. Because Si_3N_4(0001) is aligned with the Si(111) substrate, if the Ge islands grown on Si_3N_4(0001) have the same epitaxial relationship, then the Ge crystallites should align with Si(111), and Ge islands have (111) top surfaces and {113} facets as well [15]. The role of surfactant Sb is revealed after annealing the above sample under Sb flux at 550 °C for several hours. Although no drastic change of the island morphology is observed, new reconstructions on the facets are found due to the incorporation of Sb into the Ge surface region. The original Ge(111)-c(2×8) turns into Ge(111)-(2×1)–Sb. A triangular (111)-(2×1) top surface formed by three domains on the islands can usually be seen, as shown in figure 4. On the side walls of the island, the Ge(113) facets show a (2×2) periodicity. Zahl *et al* have reported an Sb-induced (2×1) LEED pattern on flat Ge(111) surfaces [16]. Also, Sb-induced (2×2) reconstruction has been found by Dabrowski *et al* [17] on Si(113) surfaces. The atomic features of the reconstruction

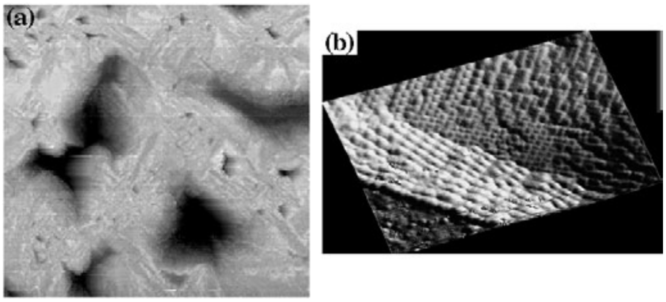

Figure 5. (a) The surface of an amorphous silicon nitride film grown on Si(001). Scanning area: 195×190 nm^2. (b) An atomic image of the bottom of a pinhole. Scanning area: 30×30 nm^2.

that we obtained on Ge are very similar to what they obtained on Si. Therefore, Sb seems to form the same surface reconstruction on Ge(113) as on Si(113).

The role of Sb in the subsequent Ge deposition has also been studied. After depositing an additional 180 nm of Ge on the surface, it is found that on some higher islands the (111) top facets shrink, so these islands are only composed of high-index side walls. Our previous studies [3] showed that without Sb the (111) top facets increase as the aligned Ge islands grow and coarsen, and become the dominant features on the overlayer surface. Here, the presence of Sb is favourable for the extension of high-index (113) facets rather than the top (111) facet of Ge islands.

3.2. Ge growth on SiN_x/Si(001)

Due to large lattice mismatch between Si(001) and Si_3N_4 crystal faces, it is impossible to grow crystalline silicon nitride on Si(001). Rather, an amorphous SiN_x film is formed after nitridation. The STM image shows no terraces or steps and ordered structure on the surface, as seen in figure 5. A diffuse LEED observation also confirmed the amorphous structure of the SiN_x film. Our XTEM observations indicate that the saturation thickness of the nitride films is about 1.5–2.5 nm, which is a little thicker than the crystalline Si_3N_4 film grown on Si(111). Although most of the surface area of the amorphous film is quite flat, there are pinholes present on the surface. The area density of pinholes is about 100 μm^{-2}, and the large pinholes have a diameter of about 50 nm and a depth up to $\sim$7.5 nm. This indicates that some pinholes penetrate through the SiN_x film and etch into the Si substrate. An STM image taken at the bottom of a pinhole also shows ordered atomic structure as seen in figure 5(b), which is probably the structure of the exposed Si substrate. When Ge is deposited on SiN_x film, the Si substrate exposed in the pinhole areas might serve as the seed for the epitaxial growth of Ge.

The growth of Ge on amorphous SiN_x film also proceeds in a 3D islanding mode. The LEED and TEM measurements indicate that the Ge overlayer is a polycrystalline film consisting of randomly oriented crystallites. Similar to the case for Ge growth on crystalline SiN_x film, the sample surface is covered by many round-shaped clusters after 20 nm Ge is deposited, as shown in figure 6(a). The smaller islands have a rounder shape than the large ones. As the islands grow larger, facets such as (111), (001), {113} and other high-index facets appear on the surfaces of the islands. When more Ge (40 nm) is added, the islands grow further, as shown in figure 6(b). Now, the {113} side walls become the dominant facets on the islands. The area density of Ge islands is about 2500 μm^{-2}, much larger than that of pinholes, so the islands cover all the pinhole areas. The atomic structure on the top facets of a small fraction of islands

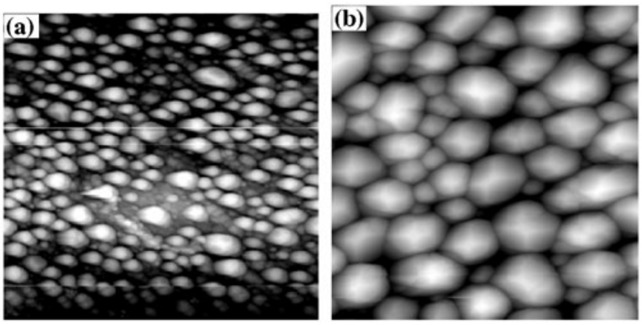

Figure 6. STM images of (a) 20 nm Ge and (b) 60 nm Ge deposited on SiN_x/Si(001). Scanning area: 300×300 nm^2.

is Ge(001)-(2 × 1). These Ge islands aligned with the Si(001) substrate very probably grew out of the pinholes. The reconstruction on {113} side walls is (2 × 2).

After the sample was annealed at 550 °C under Sb flux for 2.5 h, the area of (001) facets increased. On the top of the Ge islands, the (2 × 1) reconstruction remains, and it might be constructed with Sb since the dimers are now exclusively symmetric. Previous work [18] has shown that upon depositing a monolayer of Sb the Ge dimers are broken, and the Sb atoms dimerize on the top of the Ge layer, forming dimer rows composed of symmetrical Sb dimers perpendicular to the original Ge dimers. Eaglesham *et al* [19] reported an increase of area of (001) versus {113} after a long annealing time of up to 10 h with the presence of Sb. In our experiment, the area of (001) also increases, although not so significantly as that in [19].

The role of Sb in the subsequent Ge deposition on SiN_x/Si(001) is different from that in the case of deposition on SiN_x/Si(111). After the additional deposition of 90 nm Ge on the Sb-terminated Ge/SiN_x/Si(001), some islands with large (001) facets appear. In figure 7(a) we can find two islands with large flat (001) terraces on the top. It is also found that some island facets have smaller inclinations to the (001) plane than that of {113}. Therefore, the surface morphology appears flatter than the previous one. Figure 7(b) is obtained after additional deposition of 240 nm Ge on the sample surface. Near the middle of the image an island with a Ge(001)-(2 × 1)–Sb top terrace of area $\sim 68 \times 84$ nm^2 can be seen. The symmetric dimers indicate that Sb atoms 'float' on the surface during the process of growth. The four side walls of this island are inclined much closer to the (001) plane than {113} facets. On the left side of the flat island a pyramidal island is found. Figure 7(c) is the magnified image of the island. The side walls of the pyramid are not perfect facets but are composed of stepped (001). Their inclinations with the (001) surface are in the range 5°–7°. Some regions of the side walls have ordered step structures with a periodicity of ∼2.1 nm. These areas can be considered as the Sb/Ge(11n)-(2 × 1) surface with $n \geqslant 11$. In our previous investigation [3] where Sb was not used, we observed that all (001) facets shrink during the Ge growth. Here, with an Sb surfactant layer, only some of the top (001) facets shrink, while others maintain a relatively large area.

The influence of Sb on the subsequent Ge growth shows strong orientation dependence. This can be understood by the change of the surface energy anisotropy of the crystallites. Eaglesham *et al* evaluated the surface energy $\gamma(\theta)$ as a function of orientation near Ge(001) with and without the Sb surfactant [19]. Their results showed that, after Sb termination, the surface energy of (001) drops significantly, so the (001) facets become more energetically favourable with respect to the (113). During the subsequent Ge growth on the Sb/Ge/SiN_x/Si(001), the fact that the (001) facets are greatly enhanced suggests that the total surface energy of the Sb-terminated Ge islands plays a dominant role. After Sb deposition, the surface energy

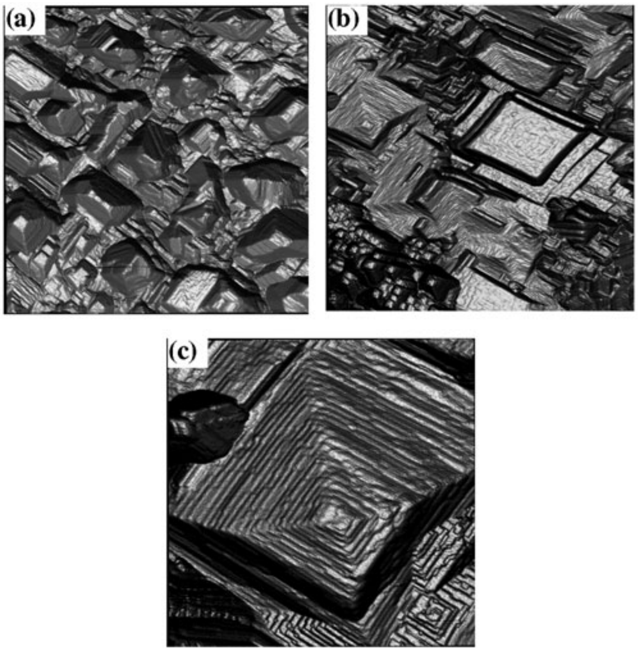

Figure 7. STM images obtained after depositing (a) 90 nm Ge, and (b) 330 nm Ge on Sb/Ge/SiN_x/Si(001). Scanning area: 300 × 300 nm^2. (c) The magnified image of an island observed in the left-hand part of (b). Scanning area: 100 × 100 nm^2.

anisotropy of the Ge islands changes to the advantage of (001) facet growth, so the original (001) facets grow quickly. In the meantime, other facets such as (113) pass gradually towards stepped (001) or those facets which are inclined very close to (001), like the side walls of the island shown in figure 7(c). As for the Ge growth on Sb/Ge/SiN_x/Si(111), the surface energy of (111) is always larger than that of (113) before and after the termination of Sb. Therefore, the growth of (111) facets cannot be enhanced during the subsequent growth. These different effects of Sb on the growth of Ge overlayers might be useful if one wishes to control the size, shape, and uniformity of self-organized Ge quantum dots grown on the surfaces of SiN_x/Si.

4. Conclusions

We have studied the influence of surfactant Sb on the islanding growth of Ge on SiN_x/Si(111) and SiN_x/Si(001) surfaces. After the deposition of 1 ML Sb on the pre-formed Ge islands, the surface energies of Ge facets are changed, and the subsequent growth of Ge leads to different morphologies of Ge islands compared with the situation without Sb. In the case of Ge on SiN_x/Si(111), Sb does not favour the growth of (111) top facets to flatten the surface. However, in the case of Ge on SiN_x/Si(001), (001) facets are enhanced and become the dominant facets on the surface, leading to earlier coalescence between islands and forming a flatter surface.

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