# Microscopic study of the surfactant-assisted Si, Ge epitaxial growth

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(Received 18 May 1992; accepted for publication 21 August 1991)

The Sb-assisted Si, Ge epitaxial growth processes have been studied using high resolution photoemission. It is found that the initially ordered Sb monolayer on the Si(100) and Ge(100) surfaces occupies the epitaxial sites and fully saturates the surface dangling bonds. This results in a reduction of the surface energy. During the growth process, the Sb atoms and the deposited Si, Ge atoms change their positions. Sb atoms segregate to the growth front to form a new ordered layer while leaving the uniform epitaxial Si, Ge layer behind.

High quality growth of epitaxial Si, Ge film has attracted much attention recently. The driving force mainly comes from the potential application of SiGe alloy and Si, Ge strain layer structures in new generation semiconductor devices, such as high speed devices[1] and optoelectronics applications.[2] It is also of fundamental importance to understand the epitaxial growth process in general, including the interplay among surface, interface free energy, and lattice strain relief. For the Si/Ge system, Ge can grow on the Si(100) surface following the Stranski–Krastanov mode. In contrast, Si starts islanding from the beginning of growth on the Ge(100) surface. In order to achieve uniform growth, growth temperature has been pushed lower and lower in various growth techniques. However, the achievement of the overlayer uniformity is based on the sacrifice of its crystallinity. Therefore, there is an urgency to look for other strategy. Recently, it has been demonstrated that when the growth front is terminated by a specific third species, the so-called surfactant, which is energetically favored over either Ge or Si termination and always moves with the growth front, the Si and Ge growth mode can be dramatically changed. There, three-dimensional (island) growth has been converted into two-dimensional (layer) growth up to a reasonable thickness that is much larger than the "critical thickness" and uniform epitaxial Si, Ge layer growth can be realized.[3] A number of atoms, such as As, Sb, and Te, have been used as surfactants.[3–5]

Although the surfactant-assisted Si and Ge epitaxial growth process is under active investigation, the growth mechanism is not well understood yet. The goal of this work is to provide a microscopic description of such a growth process at the atomic scale. Here, we carefully study the growth process at various stages, paying special attention to the structural and electronic properties, particularly the role of the surfactant during the entire growth process. Sb was used as a prototypic surfactant to examine such a growth process because Sb/Si(100) and Sb/Ge(100) have long been viewed as model systems and studied rather intensively. Also, Sb is relatively easier to handle with precise control compared with As, so that a quantitative study is feasible. We found that the ordered Sb layer occupies the epitaxial sites and saturates the surface dangling bonds of both Si(100) and Ge(100) surfaces, and thus reduces the surface energies. During growth, Sb and incoming species exchange their positions. As a result, Sb moves to the growth front to form a new ordered layer, while leaving epitaxially grown film behind.

The experiment was carried out at the Stanford Synchrotron Radiation Laboratory on beam line I-2 with a 6-m toroidal grating monochromator. An ultrahigh vacuum VG ADES400 angle-resolved system equipped with a hemispherical analyzer was used with combined resolution of about 0.25 eV. The Si(100) samples were chemically cleaned and etched in 48% HF solution for a fraction of a minute before being introduced into the system. The samples were then prebaked at ~500 °C for about an hour and annealed to ~900 °C to drive away hydrogen. The Ge(100) samples were cleaned by thermal annealing at ~800 °C. Sharp two-domain $(2\times1)$ diffraction patterns were observed from the low energy electron diffraction (LEED) optics on these surfaces. Sb and Ge were evaporated from tungsten filament evaporators, and Si was evaporated with an electron beam evaporator. Thorough outgassing was performed prior to deposition. The pressure was kept in $10^{-10}$ Torr range during sample cleaning and evaporation with a base pressure around $1\times10^{-10}$ Torr. No trace of contamination was found within the sensitivity of photoemission.

The Si, Ge heteroepitaxial growth process is as follows: after the Si(100) [Ge(100)] surfaces were thermally cleaned, a couple of monolayers of Sb were deposited on the surfaces at room temperature. The interfaces were then annealed to ~500 °C. This treatment leads to formation of an ordered Sb monolayer residing on the top surfaces. Ge(Si) was then deposited onto the structures at room temperature followed by thermal annealing at ~500 °C or at elevated temperature (~500 °C). The observed LEED pattern and angle resolved valence band photoemission spectra indicate that the growth structures are well ordered and occupy the epitaxial sites.

Let us first examine the substrates at various stages during the epitaxial growth process. Figure 1 shows the substrate Si 2*p* and Ge 3*d* spectra, together with the decomposed components using least-square fitting. The spectra have been moved to correct the band bendings of the substrate. The spectra of the clean surfaces exhibit obvious shoulders (*S*) on the low binding energy side relative to the main (*B*) peaks. They have been identified as surface core-level shifts, and it is generally agreed that they are associated with dangling bonds from the top surface atoms.[6,7] When several monolayers of Sb were deposited on