Atomic Assembly of Germanium on Silicon

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Abstract

The formation of germanium structures during growth from hydride gas sources can be observed with near atomic resolution in an elevated temperature UHV STM. A rather complete account can be given of the growth of silicon on Si(001) from disilane, and atomistic modelling can be applied to the structures seen by STM to give confident interpretation of the results. The growth of germanium on Si(001) at temperatures up to 800 K follows a similar path for the first few monolayers, after which the strain is elastically relieved by trenches first perpendicular to the dimer rows and then parallel to them, and eventually by a combination of facetted pits and clusters, both of which nucleate heterogeneously at surface defects. Understanding these processes is crucial to controlling the size distribution of Ge/Si quantum structures.

Introduction

With the inexorable drive towards smaller and smaller electronic devices, the fabrication of structures below 100 nm remains a challenge for which no presently available lithographic technique is suitable for industrial use. For example, there are no transparent materials for lenses at short enough ultraviolet wavelengths. To make smaller structures it will be necessary to use either a new kind of lithography, or to use atom manipulation techniques, or to use self assembly of atoms, or perhaps some combination.[1] For any technology that grows out of the present silicon-based industries, the use of germanium in combination with silicon has great attractions of compatibility. An understanding of how germanium grows on silicon may prove invaluable in developing ways of producing quantum sized structures that will be useful in future sub 100 nm technologies.

Some of the stages of the growth of germanium growth from a hydride source (GeH₄) on silicon are illustrated in Figure 1. The horizontal axis of the map indicates the amount of coverage, up to 10 monolayers (averaged over the surface). The vertical axis denotes the temperature of the substrate. Three temperature ranges are denoted: below 600K, between 600K and 700K, and above 700K. The data on which this map is based were obtained by in situ observation of the growth in a variable temperature UHV STM (JSTM-4500XT).[2] The STM was equipped with a gas source which enabled germane to be admitted to the microscope chamber while the sample was being imaged at the temperature of interest. For each experiment the starting substrate was a sample of Si(001) which had been prepared to give a clean dimer reconstructed surface.

The first monolayer

The first monolayer of growth proceeds in a manner almost indistinguishable from gas source molecular beam epitaxy of silicon on Si(001). That has been studied in detail, both on surfaces quenched from the growth temperature,[3] and also in situ in real-time at growth temperatures using the same JSTM-4500 XT as the one used for the germanium growth images presented in this paper.[4] It has proved possible to relate the experimental observations to atomistic modelling, in order to give confident interpretation of the structures seen in the images, and also to provide accurate estimates of the energy of each of the structures involved in the growth process.[5] Disilane adsorbs and dissociates to yield SiH₂ groups and hydrogen. Above 470K these groups diffuse and two such groups can combine and lose half their hydrogen to form a monohydride dimer, initially with the same orientation as the substrate dimers. This hydrogenated dimer has to lose its hydrogen and rotate to the correct orientation for the growth of the next layer, and a mechanism has been proposed whereby these two processes could happen together. A square structure has been observed, which is believed to act as a nucleus for the subsequent growth of dimer strings on the surface.[6] The strings then grow
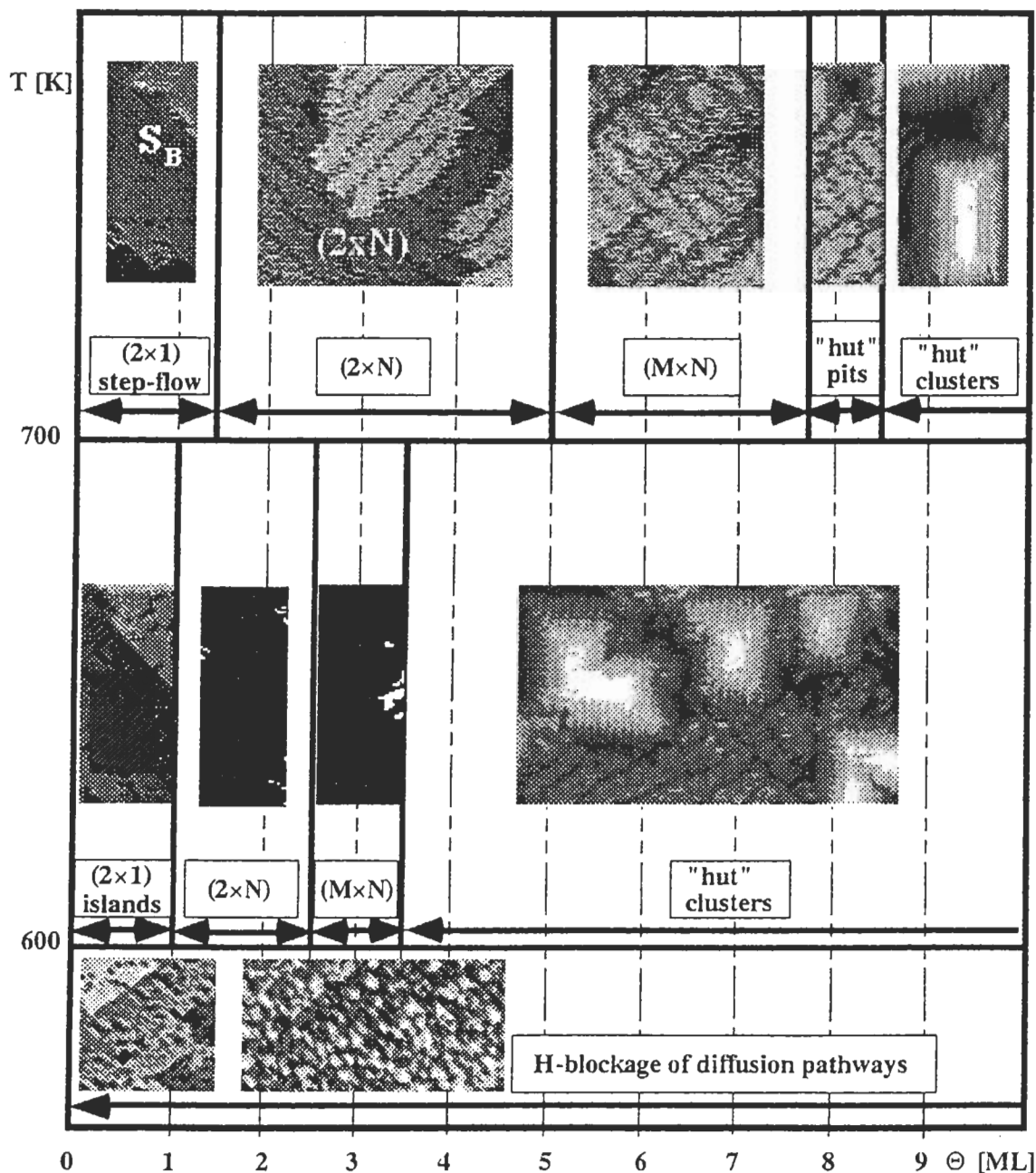
Fig.1   The main stages of Ge/Si(001) growth from GeH₄ in the pressure range 10^{-6} Pa $< P < 5 \times 10^{-5}$ Pa.[2]

by the addition of pairs of dimers to their ends. The observation of many of the same features and processes in the first monolayer of germanium growth on Si(001) is a strong indication that the mechanisms are the same. For example, similar square features are seen.[2] In filled-states images these appear as a doughnut shape with four nodes along ⟨010⟩ directions. In empty states-images the orientation of the nodes is rotated through 45°, to ⟨110⟩ directions. Detailed modelling

accounts for these squares as four non-hydrogenated silicon atoms bonded to each other and to substrate silicon atoms on two adjacent dimers. The lowest energy configuration is with the atoms arranged not in a symmetrical square, as the images suggest, but in an arrangement which approximates to a rhombohedron albeit with the atoms not quite lying in a plane. There are two degenerate geometrical configurations, each with two degenerate electronic configurations, and the

atoms flip between these sufficiently fast that an average is seen in the STM images. Simulations of the filled- and empty-states images averaged over the degenerate configurations are fully consistent with what is seen experimentally. The structure presents what look like two incipient B-type steps on opposite sides, and these provide excellent sites for formation and growth of dimer rows.

A key difference between solid source MBE and gas source MBE arises from the presence of hydrogen on the surface.[7] If the temperature is too low for hydrogen to desorb, it inhibits surface diffusion and can lead to rough growth. At intermediate temperatures it can block growth at steps, and therfore promote island growth in preference to step flow growth. The hydrogen desorption temperature from germanium surfaces is about 50K lower than from silicon surfaces, but because of differences in the desorption from steps mixed step flow and island growth are more prevalent with germanium than with silicon. Depending on the germaine flux, two dimensional growth of even one or two layers of germanium from germane does not occur below about 600K.

The next few layers

The most fundamental difference between the growth of germanium on silicon and the growth of silicon on silicon arises because of the different lattice parameters, the germanium lattice parameter being 4.2% greater. This means that after the first layer has grown, subsequent layers experience increasing lateral strain. This strain energy can be elastically reduced by omitting dimers in subsequent layers, the energy cost of the missing dimer defects being offset by the reduction in elastic strain energy. The resulting defect structures are illustrated in Fig. 2. Initially the strain is relieved by missing out occasional dimers in a row, so as to allow the remaining dimers to expand somewhat along the row direction. There is a tendency for missing dimers in adjacent rows to line up to create dimer vacancy lines (DVL's). This structure can be described as $(2 \times N)$, where the 2 arises because of the dimerisation, and the N describes the average spacing of the DVL's. The value N depends on the temperature and the coverage; at 620K it has an initial value $N \approx 10$ at a germanium coverage $\theta = 1.5$ ML, at which the DVL's first appear, and decreases to its minimum value of $N \approx 7$ with the addition

of one more monolayer of germanium. When no further strain can be alleviated by DVL's, a second mechanism begins to operate, in which the strain across the dimer rows is reduced by allowing whole dimer rows to be missing; thus creating dimer row vacancies (DRV's). These are never entirely regular, but they give rise to a structure which can be described as $(M \times N)$, where M describes the average spacing of the DRV's. At 620K it has an initial value $M \approx 14$ at a coverage $\theta = 2.5$ ML, when they first appear, and decreases to its minimum value of $N \approx 9$ with the addition of a further monolayer of germanium. At higher temperatures there is a general shift to higher coverages for each transition, so that at 700K the DVL's first appear at $\theta = 2$ ML with a period $N \approx 13$ and the DRV's are delayed until about 5 ML coverage.

The onset of three-dimensional growth

Eventually a coverage is reached at which the strain can no longer be relieved by combinations of missing dimers, and at that point fully three-dimensional growth occurs. At the lowest growth temperatures (around 600K) this occurs at a coverage of less than 4 ML. Germanium atoms assemble and form what have come to be known as hut clusters, because of their characteristic appearance in the STM.[8] They have {501} facets, and are generally longer in one direction than another, so looking like huts with roofs sloping at an angle of $11.3°$. The reconstructed atomic rows can be resolved on the facets of the huts. The huts always nucleate at defects in the surface, and never on a perfect terrace. Although the DVL's and DRV's run in basically <110> directions, local irregular defect areas eventually adopt <010> edges, which provide nucleation sites for the huts. Nucleating huts sometimes straddle DRV's and form with a central cleft, but this rapidly fills in to create a complete hut, which are intitially pyramidal with a square base. The clusters can adopt {501} facets from the very earliest moment of formation, indeed plenty of examples have been seen of clusters which are below the minimum possible size for a pyramid, and yet which exhibit the rows characteristic of {501} facets.[9]

At higher temperatures the coverages at which the transitions occur generally increase, and by about 700K this enables an utterly new phenomenon to occur, which had been

predicted theoretically[10] and was revealed experimentally by the *in situ* observations. After the DVL + DRV structure is fully developed, but before hut or pyramids form, pits occur in the surface with an inverted pyramid structure.[11] They have the same {501} facets as the huts, once again characterized by the rows on the faces, but they are concave in the surface rather than protrusions. They are short lived, which is probably why they had not been observed in *ex situ* experiments; at 700K they exist only for coverages close to $\theta \approx 8$ ML. When they occur, they invariably act as nucleation sites for subsequent huts, which are seen to form next to them generally sharing a common {501} facet.

Subsequent cluster growth

In order to exploit the clusters for electronic or optoelectronic applcation, it is essential to understand what determines their eventual size, and what the constraints on size distribution are. The growth of huts seems to be diffusion limited,[12] with the strain concentration at the base of the pyramids acting as a barrier to the transport of atoms from the wetting layer to the faces of the huts,[13] where growth probably occurs by nucleation and flow of steps on the {501} facets themselves.[11, 12, 14] Ostwald ripening is not a prevalent mechanism. Annealing at temperatures above 770K leads to a gradual replacement of huts by larger clusters.

Detailed studies have been made of large numbers of germanium clusters grown by CVD on Si(001) at 870K.[15] The clusters fall into two different types: pyramids with square bases and {501} facets, and domes with multiple facets (including {311}) and irregular but more rounded bases. The size distributions of these two shapes form into two groups which scarcely overlap, suggesting that each represents an equilibrium form but that there is an energy barrier to change from one form to the other which can be overcome by a sufficiently large fluctuation in the number of particles in either structure. The evolution of the bimodal distribution of island sizes during growth has also been observed by *in situ* UHV transmission electron microscopy, which confirms that the islands can develop a stable and well-defined size range.[16]

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