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Express Letter

A Novel Growth Approach of Ultrasmall Ge and Si Nanoclusters on a Si(100) Substrate without a Wetting Layer

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Growth of ultrasmall Ge and Si nanoclusters has been achieved on a Si(100) substrate in the use of Xe buffer layer. The temporary use of Xe buffer layer, which has the low surface free energy, leads to nanoclusters formation on Si(100) due to the indirect interaction between deposited Ge or Si atoms and a Si(100) substrate. The formation of Ge and Si nanoclusters on Si(100) surface without a wetting layer was confirmed by the scanning tunneling microscope observation. Ge nanoclusters are much smaller and denser than that are grown by the Stranski-Krastanov mode. [DOI: 10.1143/JJAP.42.L1232]

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Growth of nanoclusters has been of great interest in recent years at both a fundamental and applied level. Their potential applications range nanoscale electronic and optical devices, high-density magnetic memory, and biomedical sensors.[1–3] Namely, this quasi 0-dimensional quantum dot (QD) is constrained in all three dimensions due to small length scale and thus the physical properties of the system are dominated by quantum effects.[4] Especially, nanostructured materials on a Si substrate are of important because of the future demand of the miniaturization and the integration of Si-based devices. However, practical applications are currently limited by the fact that each nanocluster-substrate combination requires specific growth technique with often very little control on the size or spacing of nanoclusters. In many cases, there is no clear growth process to produce nanoclusters in both a mass production and an aligned scale. A novel method that can synthesize nanoclusters of any materials on any substrates will be pivotal in practical level applications.

In phenomenological island growth mode (or Vollmer-Weber (VW)) the interaction between neighboring layer atoms should be stronger than that between substrate and layer atoms. It means that the low surface free energy (SFE) of a substrate is generally required for island growth. Thus, a key concept in our experiment is the modification of the SFE of a substrate using an inert gas that has normally very low SFE. This process interrupts the normal growth process and artificially makes a necessary condition of the nanoclusters formation. To promote cluster formation and to free the system from kinetic and stress constraints when depositing a source material on substrate, the technique of buffer-layer-assisted growth (BLAG)[5] is utilized where a temporary buffer layer of an inert gas is frozen on the surface of a substrate before deposition of a source material (see Fig. 1). The substrate temperature then is slowly raised to room temperature (RT) to remove the buffer layer, allowing the nanoclusters to be softly landed on the substrate. In fact, BLAG method has been tested on the various systems, such as Ag on a silicon surface and metals on metals.[6] Because deposited atoms form on the buffer layer and then coalesce to form clusters as the inert gas layer desorbs, it is known to be possible to preserve atomic scale pristine surfaces.[5] Recently, Zhang *et al.* in our group proposed and developed this method to the buffer-layer and charging (BLaC) that can grow even better size and higher density distribution of QDs on any substrates.[7] In this Letter, we present the growth of Ge and Si nanoclusters on a Si(100) substrate, which are typical examples of semiconductor on semiconductor system. We have succeeded for the first time in the growth of the ultrasmall Ge and Si nanoclusters without a wetting layer. The absence of a Ge and a Si wetting layer was clearly observed in scanning tunneling microscopy (STM) measurements.

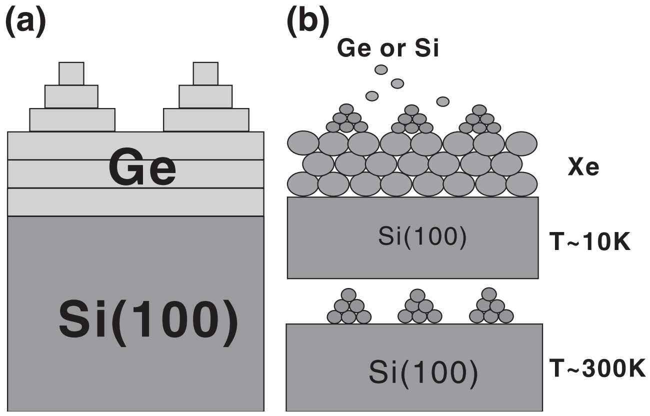

Fig. 1. Schematics of (a) SK island growth mode and (b) BLAG method. A frozen Xe layer in BLAG is used as a buffer before deposition of Ge or Si sources on a Si(100) substrate.

Experiments were carried out in an ultrahigh vacuum (UHV) with a base pressure of $\sim 2 \times 10^{-10}$ Torr. The system consists of two parts, which are a molecular beam epitaxy (MBE) growth chamber with cooling and heating facilities for low temperature growth ($10 \sim 300$ K) and an *in situ* Omicron STM for morphology. We used a graphite crucible mounted in *e*-beam evaporator for Ge sources and a PBN effusion cell (K-cell) for Si sources. The deposition rates were determined by *ex situ* Rutherford back scattering measurements on deposited source materials on a graphite foil. The deposition rate was ~ 0.14 ML for Ge and ~ 4.3 ML for Si (1 monolayer (ML) $= 6.87 \times 10^{14}$ atoms/cm^2). Several 7.0 mm $\times$ 3.0 mm $\times$ 0.2 mm Si samples were cut out from *p*-type Si(100)wafers with resistivity $0.3 \sim 0.4\ \Omega\cdot$cm. A Si(100) 2x1 surface reconstruction was obtained by repeated direct current flashing Si sample up to 1300 K after degassing for overnight at ~ 873 K and checked by

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STM.

A clean Si substrate was transferred to a MBE growth chamber and cooled down to $\sim$ 10 K under UHV. Then a Xe buffer layer about 30–50 Langmuirs (L) was exposed through a leak valve from a pure Xe bottle ($1L = 10^{-6}$ Torr·s). The condensed 1 ML of Xe corresponds to 5.5 L Xe exposure.[8] Next, a flux of pure Ge or Si atoms was deposited on top of the condensed Xe layer. These atoms are highly mobile on top of Xe layer due to the low surface free energy of Xe, and easily diffuse to form three dimensional nanoclusters. Finally, the substrate was immediately warmed up to $\sim$ 300 K to remove the Xe buffer layer. This procedure leads a soft landing of the nanoclusters to a Si(100) substrate. Morphology of nanoclusters was confirmed by STM at RT.

Ge/Si(100) is chosen as a heterogeneous semiconductor system. First, we tested Ge islands-formation on Si(100) that is well known as a Stranski-Krastanov (SK) growth mode example.[9–11] Figure 2(a) show the STM data of a typical layer-by-layer growth mode at Ge $\sim$ 2.0 ML, which is less than the critical thickness ($\sim$ 3.0ML) of Ge coverage. The growth results at a Ge coverage ($\sim$ 1.2 ML) are well agreed with that of previous report (see inset of Fig. 2 (a)).[12] Figure 2(b) shows the STM image of Ge nanoclusters on Si(100) after the deposition of $\sim$ 0.5 ML equivalent of Ge atoms on a 6 ML Xe buffer layer. The image of Ge nanoclusters was taken at RT after removing the Xe-buffer layer by sublimation. In fact, as evidenced in Fig. 2(a), it would not be possible to observe any Ge nanoclusters formation in the SK growth regime with such a small amount of deposited Ge atoms.[13–15] However, the Ge nanoclusters grown by the BLAG method clearly appear on a pristine Si surface along with on three-step edges (more clearly in inset of Fig. 2(b)) in the background of the STM image. The equivalent Ge coverage derived from the nanoclusters size and density confirms that almost all Ge adatoms exist in the form of nanoclusters. It proves that the mediation of the Xe buffer prevents direct interactions of deposited atoms with the substrate and *no strained Ge wetting layer* forms between the substrate and the nanoclusters.

Figure 3 (a) shows a typical SK Ge-island with a base size of $\sim$ 60 nm, which formed on top of Ge wetting layer with the Ge coverage of $\sim$ 3.2 ML. It is well known that SK Ge islands-shapes are various like hut, pyramid, and dome

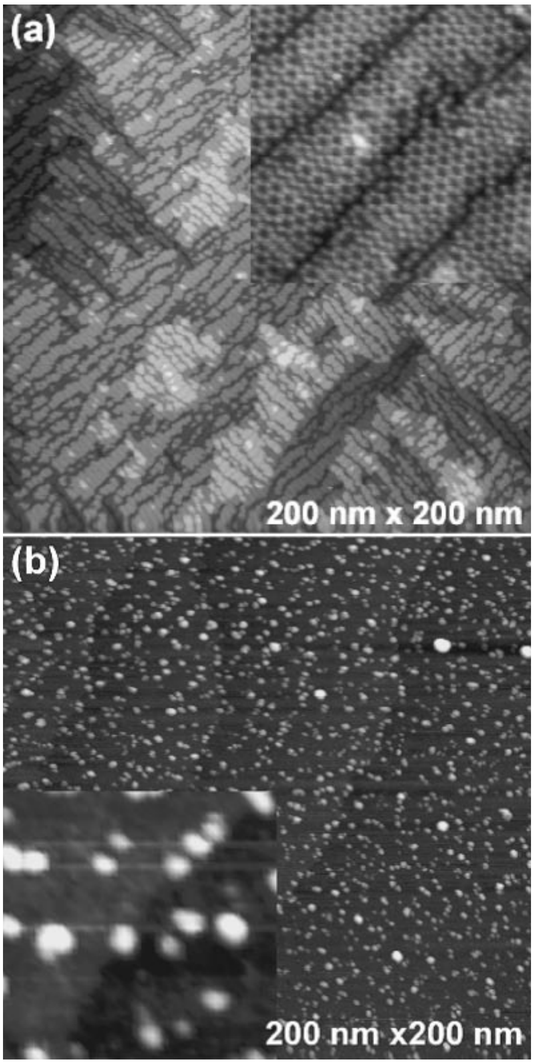

Fig. 2. STM images of Ge growth on Si(100) without/with Xe buffer layer: (a) A typical layer-by-layer growth of Ge/Si(100) below the critical Ge coverage ($\sim$ 3.0ML) and (b) Ge nanoclusters on Si(100) in BLAG. Ge coverages are repectively $\sim$ 2.0ML (inset Ge $\sim$ 1.2ML) and $\sim$ 0.5ML.

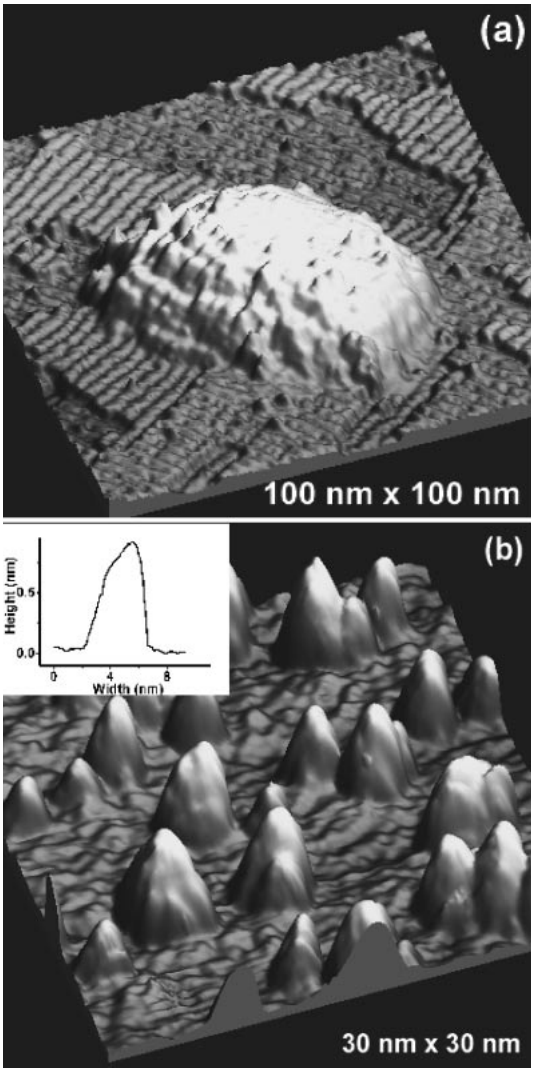

Fig. 3. STM images of (a) a typical Ge island grown by SK mode just before turning 3 dimensional dome shape (Ge $\sim$ 3.2 ML) and (b) Ge nanoclusters grown by BLAG with a line profile (Ge $\sim$ 0.5 ML).

depending on growth conditions. The back ground of STM data also clearly indicates a Ge wetting layer, which is known as two domain $2 \times n$ structures. On the other hand, STM studies in BLAG indicate that Ge nanoclusters are shaped like rock mountain or dome as shown in Fig. 3 (b). The average width and height of those nanoclusters are respectively ~ 3 nm and ~ 0.6 nm with a narrow size distribution. The size of Ge nanoclusters is remarkably smaller than SK Ge dots which normally have a width of $60 \sim 200$ nm and a height of ~ 12 nm for pyramid or dome shaped islands on top of a wetting layer.[13)] Even the hut structure Ge islands are more than ~ 40 nm laterally and $1 \sim 3$ nm in height.[13,16)] The density of the nanoclusters is deduced from Fig. 2(b) to be about 5×10^{12} cm^{-2}; i.e., more than 3 orders of magnitude higher than that of SK islands with a density of $10^8 \sim 10^9$ cm^{-2} in dome or pyramid shapes, and 2 orders of magnitude higher than hut clusters.[13,16,17)] Our results are comparable with that of Shklyaev *et al.*'s report on the formation of an ultrasmall size (6 nm) and a high density (3×10^{12} cm^{-2}) of Ge nanoclusters on Si surfaces covered with an ultrathin SiO_2 layer.[18,19)] They suggested a possible type I band alignment in Ge/Si system.[19)] Thus, it is very encouraging because the size of Ge nanoclusters is much less than the observable length regime of the quantum confinement effects, which is about the order of 10 nm. It means that the characteristics of these quasi-zero-dimension nanoclusters without a wetting layer suggest a better carrier confinement, which is desirable for applications in Si-based optoelectronics. The growth of the size-controlled Ge nanoclusters and the photoluminescence of multilayer structures will be done near future and published elsewhere.[20)]

Since the growth of Si on Si surfaces is governed by the two dimensional layer-by-layer mode,[21,22)] the Si nanoclusters formation on Si is basically not possible with normal growth method. It has been only possible to grow the Si islands on Si surfaces with the modification of the growth mode using Ge or ultrathin oxide layer.[23–25)] We have tackled to grow the Si nanoclusters on Si(100) with the same experimental scheme. Figure 4 shows the Si nanoclusters formation on S(100) with ~ 1.0 ML Si coverage. Though Si nanoclusters are not clear as much as that of Ge, and the considerable size of Si nanoclusters is clearly shown with the two step edges of a Si substrate. The average width and height of Si nanoclusters (1.0 ML Si deposition) are respectively ~ 3 nm and ~ 0.5 nm within experimental errors. Interestingly, we could not observe Si nanoclusters formation in lower Si coverage. It might be because Si nanoclusters easily diffuse to the surface at RT in case of the lattice-matched system and thus have a less chance to hold the nanoclusters.

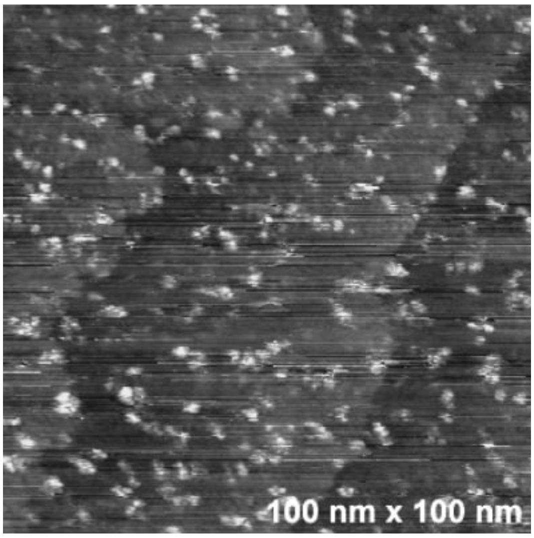

Fig. 4. STM image of Si nanoclusters on S(100) with ~ 1.0 ML Si coverage. The Xe buffer layer was ~ 6 ML.

In summary, we have successfully fabricated exceptionally small Ge and Si nanoclusters on Si(100) using a Xe buffer layer. As expected, we observed no wetting layer formation in BLAG growth. This growth method may be applicable for (almost) any materials on any substrates.

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