



Surface Science Letters

# Fabrication of Ge nanoclusters on Si with a buffer layer-assisted growth method

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Received 14 July 2003; accepted for publication 22 September 2003

## Abstract

Size selectable Ge nanoclusters are formed on Si using a buffer layer-assisted growth method. A condensed inert gas layer of xenon, with low surface free energy, was used as a buffer to prevent direct interactions of deposited Ge atoms with Si substrates during Ge nanocluster growth. The scanning tunneling microscope studies indicate absence of a strained wetting layer between Ge nanoclusters. These nanoclusters are substantially smaller and denser than the Ge hut clusters that are formed with the normal Stranski–Krastanov growth mode. The morphology of the nanoclusters can be tuned over a wide range, which is very desirable for studying the three-dimensional confinement effect.

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**Keywords:** Scanning tunneling microscopy; Evaporation and sublimation; Growth; Germanium; Silicon; Clusters

Semiconductor nanoclusters, in which electrons are confined in all three dimensions, show novel physical phenomena related to dimensionality, such as an atom-like energy spectrum and quantum size effects. The growth of zero-dimensional (0-D) semiconductor nanoclusters and the utilization of their novel physical phenomena have drawn much attention recently. In view of potential applications in silicon-based optoelectronic devices [1,2], the

quasi 0-D Ge nanocluster on Si(1 0 0) system grown in the Stranski–Krastanov (SK) growth mode [3–5] has been intensively studied in the past decade. Although remarkable success has been achieved [6–8], it is still challenging to realize 0-D Ge nanoclusters on Si(1 0 0) with small, dense, and uniform dot formation. Germanium SK dots grown on Si have lateral dimensions of 20–200 nm and are 1–12 nm in height. Their larger lateral size means that quantum confinement effects are determined by the Ge width in the growth direction. Unfortunately, SK growth is initiated with the formation of a 2-D Ge wetting layer beneath the dots [9–11]. Wetting layer formation is due to the lattice mismatch

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(4.2%) between Si and Ge, which leads to a layer with built-up strain (layer by layer growth) and a relief of strain energy (3-D islands formation) when the layer grows beyond a critical thickness. This wetting layer is electronically coupled to the Ge dots increasing the structures' thickness by up to 50% thereby reducing quantum confinement effects even in the growth direction. It also acts as an additional electronic structure and reduces the electronic isolation of the dots from one another affecting device performance. To avoid wetting layer formation, an alternate growth technique is required.

A buffer layer-assisted growth method using frozen xenon was first proposed by Weaver and Waddill [12] to grow metal nanoclusters on various substrate systems. Because deposited atoms diffuse and form nanoclusters on the buffer layer, the nanocluster growth is independent of the substrate. When the nanoclusters are deposited on the substrate by warming to remove the buffer layer, an abrupt nanocluster/substrate interface is formed [12–15]. In this letter, we present the formation of Ge nanoclusters on Si(100) with the buffer layer-assisted growth method, which is the first demonstration this growth technique can be used for the formation of semiconductor nanostructures. The nanoclusters are characterized by absence of a wetting layer, small sizes, and high density compared to Ge nanoclusters that are formed with the normal SK growth method.

The growth experiments were carried out on Si(100) substrates in an ultrahigh vacuum (UHV) system with base pressure of  $2 \times 10^{-10}$  Torr. The system consists of a molecular beam epitaxy (MBE) growth chamber and an in-situ Omicron scanning tunneling microscopy (STM) for morphology analysis. A Si(100)  $2 \times 1$  surface reconstruction was obtained by flashing Si to 1200 °C.

A schematic of sample preparation with the buffer layer-assisted growth method is shown in Fig. 1. First, a clean Si(100) substrate was cooled down to 10 K under UHV. A buffer layer of condensed Xe was then formed by exposure to 20–200 Langmuirs of pure Xe gas (99.995%). According to the ion gauge sensitivity to Xe, 1 monolayer (ML) of Xe corresponds to 5.5 Langmuirs of Xe exposure (1 L =  $10^{-6}$  Torr s) [16]. Then

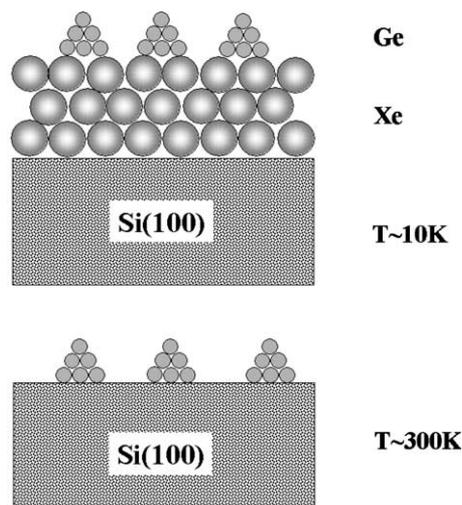


Fig. 1. Schematic of the buffer layer-assisted growth technique.

a flux of pure Ge atoms was deposited on top of the Xe buffer layer. These atoms exhibit extremely high mobility on top of the buffer layer compared to direct deposit without the buffer layer due to the low surface free energy of Xe, and diffuse to form three-dimensional nanoclusters. Finally the sample was warmed to room temperature to remove the buffer layer. This provides a gentle landing of the nanoclusters to the Si substrate. All samples were examined by STM at room temperature.

Fig. 2 shows an STM image of Ge nanoclusters after the deposition of 0.5 ML equivalent of Ge atoms on a 6 ML xenon buffer layer. The image was taken at room temperature after the xenon buffer was removed by sublimation. With such a small amount of deposited Ge, it would not be possible to see any dot formation in the SK growth regime since 0.5 ML is less than the critical thickness (the onset of dot growth occurs at 5.0 ML Ge) [8,10,11]. However, with the buffer layer-assisted growth method, the Ge nanoclusters clearly appear on a pristine Si surface along with two step edges in the background of the STM image in Fig. 2(a). The equivalent Ge coverage derived from the nanocluster size and density confirms that 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 wetting*

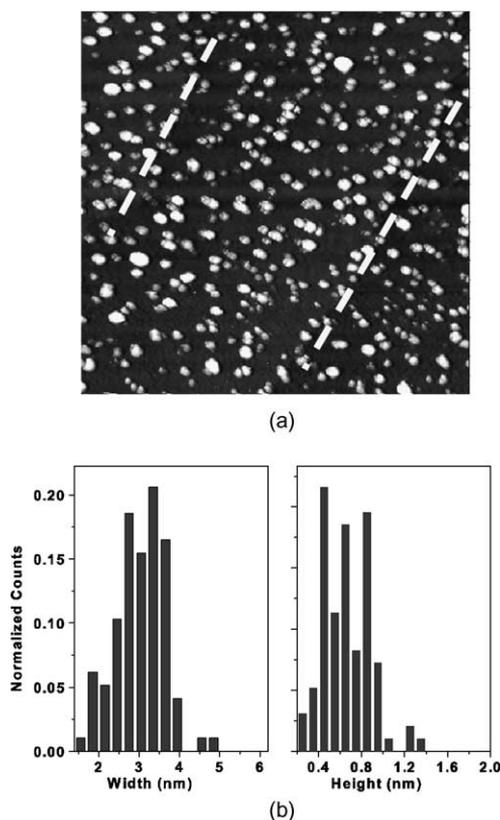


Fig. 2. Ge nanocluster formation on Si(100): (a) STM image ( $100 \times 100 \text{ nm}^2$ ) taken at room temperature following deposition of 0.5 ML Ge on 10 ML Xe buffer. Two dashed lines indicate step edges of Si surface after the nanocluster formation. (b) Size distribution for Ge nanoclusters.

layer formation in-between the nanoclusters. As shown in Fig. 2(b), the average base size of those

nanoclusters is 3 nm and the size distribution has a full-width at the half-maximum (FWHM) of 1.3 nm, and the average height is 0.6 nm with FWHM of 0.6 nm. The nanoclusters are remarkably smaller and more uniform than SK Ge dots that normally have a base size of 20–200 nm and a height of 1–12 nm with a wide size distribution for pyramid or dome shaped dots on top of a wetting layer [8]. Even the hut dots are 20–40 nm laterally and 1–3 nm in height [6,8]. The dot density is deduced from Fig. 1(a) to be about  $5 \times 10^{12} \text{ cm}^{-2}$ ; i.e., more than three orders of magnitude higher than SK dots with a density of  $10^8$ – $10^9 \text{ cm}^{-2}$  in dome or pyramid shapes, and two orders of magnitude higher than hut clusters [6–8]. The closest results to these for Ge nanocluster growth are found in the experiments in which the Ge is deposited on an  $\text{SiO}_2$  layer on Si(100) and (111) surfaces [17]. This permanent layer of  $\text{SiO}_2$  between the Ge nanoclusters and the Si substrate also prevents the formation of a wetting layer. The density is less than half that obtained with our buffer layer growth and the typical size is 6–7 nm diameter. In both the  $\text{SiO}_2$  based system and our system with Ge nanoclusters deposited directly on the Si substrate, the dimensions of the quasi-zero-dimensional clusters provide the possibility of a three dimensional carrier confinement, which is desirable for applications in optoelectronics.

Fig. 3 shows that the sizes of Ge nanoclusters can be tuned by changing the amount of deposited Ge when using the buffer layer-assisted growth method. Previous studies have shown that 4 ML Xe is sufficient to buffer the substrate [13] and 6 ML of

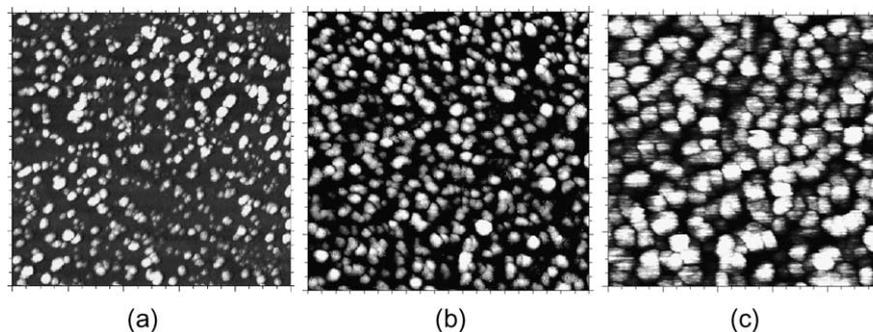


Fig. 3. Morphology evolution of Ge nanoclusters as function of deposited Ge atoms: (a) 0.5 ML; (b) 1 ML and (c) 6 ML. The thickness of Xe buffer layer is the same in all cases. All images are  $100 \times 100 \text{ nm}^2$ .

Xe is used for each case in Fig. 3. With this constant buffer layer thickness, the average nanocluster size is approximately 2.5 nm laterally and 0.4 nm in the growth direction when the Ge coverage is 0.5 ML, while at a Ge coverage of 6 ML, the nanoclusters grow to approximately 7.5 nm wide and 1 nm high. The nanocluster density increases slightly in the low coverage range of 0.5–1 ML, and then decreases at higher coverage. This is consistent with conventional MBE growth of the first monolayer where the early stages exhibit nucleation of islands followed by a steady state regime with constant island density and the later stages exhibit island coalescence. The weak coverage dependence of the nanocluster density in the low coverage regime indicates that the adatoms on the Xe buffer are mobile enough to reach the existing nuclei with very few new nanoclusters being nucleated. At high Ge coverage as shown in Fig. 3(c), coalescence of nanoclusters results in a decrease of density compared to the low coverage case.

The morphologies of the nanoclusters can also be modified by varying the buffer layer thickness. The initial shapes of nanoclusters on the buffer layer are determined by the competition between thermodynamics, which favors equilibrium structures with minimal surface areas, and kinetics that imposes constraints due to low temperature, resulting in a high density of nearly round dots. As shown by comparing Fig. 4(a) and (b), these nanoclusters enlarge as the Xe buffer thickness increases from 6 to 10 ML. This phenomenon has been ascribed to desorption-assisted coalescence [13] in which the nanoclusters have more time to

move and coalesce prior to contact with the Si substrate when landing from a thicker Xe layer. Moreover, clusters of nanoclusters develop when the Xe buffer thickness increases from 6 to 10 ML with an elongation of some nanoclusters appearing, possibly due to incomplete coalescence. Aggregation of nanoclusters into chains develops for a buffer layer thickness of 40 ML as shown in Fig. 4(c). A similar behavior was recently reported for Au nanoclusters on graphite grown with much thicker buffer layers [16]. The aggregated cluster structure can be attributed to a competition between the arrival rate of new clusters and the time needed to coalesce. Desorption of thicker buffer layers generates more cluster movement and thus leads to more pronounced cluster aggregation than the normal coalescence process.

In summary we have demonstrated the growth of Ge nanoclusters on Si without a wetting layer by using a buffer layer-assisted growth method. STM images indicate the absence of a Ge wetting layer. These nanoclusters are orders of magnitude smaller and denser than the Ge nanoclusters that are formed with the normal SK growth mode. The nanoclusters sizes are tunable in a range of 2–8 nm by changing the Ge coverage. And the nanocluster morphology changes significantly when varying the Xe buffer thickness. A thicker Xe buffer leads to formation of larger nanoclusters, and at 40 ML of Xe, significant aggregation occurs with the formation of nanocluster Ge chains. This method may be applicable to grow a variety of other semiconductor nanoclusters with a high density.

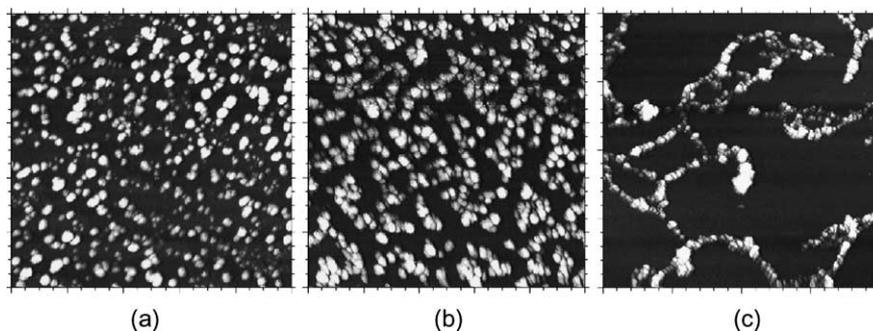


Fig. 4. Coalescence of Ge nanoclusters with increasing Xe buffer layer thickness: (a) 6 ML Xe buffer; (b) 10 ML Xe buffer and (c) 40 ML Xe buffer. The quantity of Ge deposited is the same in all cases. All images are  $100 \times 100 \text{ nm}^2$ .

## Acknowledgements

This work was supported by ORNL under the LDRD Program, managed by UT-Battelle, LLC for the US Department of Energy under Contract #DE-AC05-00OR22725, and in part by the Petroleum Research Fund, administrated by the ACS (Grant # ACS-PRF#32916-AC5).

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