Structural transition of Ge dots induced by submonolayer carbon on Ge wetting layer

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We have investigated the influence of carbon on Ge dot growth on Si(100) substrates. To modify the Ge dot structure, submonolayers of carbon were deposited on Ge wetting layers. The Ge deposited on the carbon-covered wetting layer tends to form dome structures instead of hut structures even at a substrate temperature of 500 °C. The main effect of C is to enhance a structural transition from huts to domes by influencing the configurational energy of the Ge dots. The dominant factor to determine the dot size is the substrate temperature. Accordingly, small domes with 10–20 nm in diameter were formed by combining techniques of the submonolayer C on the Ge wetting layer and low-temperature deposition. © *2000 American Institute of Physics.* [S0003-6951(00)03341-6]

Investigation of nanometer scaled materials has been a crucial subject for the development of quantum-functional devices. In particular, the Ge–Si system has been intensively studied from the viewpoint of both fundamental and applied science.[1–3] Three-dimensional (3D) Ge dot growth on a Si substrate is induced by the 4% lattice mismatch after a two-dimensional Ge wetting layer is formed, which corresponds to the well-known Stranski–Krastanov growth mode. However, the growth of Ge dots on Si shows quite complex features. Different structures, such as so-called hut, pyramid and dome structures are formed even under the same experimental conditions.[4,5] Such complexity causes difficulties in controlling the Ge dot structure. Among the observed structures, the dome structure, in principle, has an advantage for a quantum dot in terms of achieving a 3D confinement of carriers because the dome has a round shape and a quite high uniformity in size. However, a problem associated with the dome structure is the size is too large for applicable quantum confinement to occur. Typically, the size is even more than 100 nm in diameter.[6] Therefore, establishment of a new technique to reduce the dome size is an indispensable task to attain practical quantum dots in the Ge–Si system. Recently, Schmidt and coworkers[7,8] discovered a procedure which allowed to reduce the dome size. Very small domes with 20 nm in diameter were successfully formed by depositing a submonolayer C on the Si substrate. Since then, C has been recognized as an essential material for controlling Ge dot structures.

The main purpose of this letter is to deepen more insight in the C effect on Ge dot formation. We performed three-step deposition for Ge dot formation on Si substrates: (i) Ge wetting layer, (ii) submonolayer C, and (iii) Ge top layer.

Si(100) wafers were employed as substrates for the subsequent molecular beam epitaxy (MBE) growth process. After the Radio Corporation of America cleaning, the Si(100) substrates were introduced into a high vacuum chamber with a background pressure of 1×10^{-10} Torr. They were heat treated at 830 °C for 20 min to remove oxide layers. A Si buffer layer with 10 nm in thickness was deposited at 450 °C. The Ge wetting layer with a thickness of 4 Å, which is corresponding to the thermodynamically stable thickness,[9] was deposited on the Si substrates followed by C deposition. The lattice of the wetting layer is coherent to that of Si and, as a result, contains a high strain, which triggers the subsequent 3D Ge dot growth. Thus, the submonolayer C on the wetting layer is considered to directly affect the Ge dot structure. Si and Ge were deposited by a solid source MBE machine equipped with electron-beam evaporators. The carbon layers were deposited through sublimation from a heated filament. Typical deposition rates of Si, Ge, and C were 0.1, 0.05, and 6.4×10^{-5} Å/s, respectively. The mean thickness of the submonolayer C was ranging from 0.01 to 0.10 monolayer (ML). Finally, Ge top layers with 2 Å in mean thickness were deposited for the 3D dot formation. The substrate temperature was kept at 500 °C for the Ge wetting layer and submonolayer C deposition, whereas it was varied from 450 to 550 °C for the Ge top layer deposition. For comparison, pure Ge without C was deposited on the Si substrate at 500 °C followed by postannealing at 540–560 °C for 5 min. The total thickness of Ge was fixed at 6 Å for all experiments. Morphology and structure of the Ge dots thus prepared were examined by tapping-mode atomic force microscopy (AFM) and cross-sectional transmission electron microscopy (TEM).

Figure 1(a) shows an AFM image of the pure Ge dots without C. The typical hut structures with the [100] edges orientation were observed. Corresponding AFM images of Ge dots with C are shown in Figs. 1(b)–1(d). The mean thicknesses of C submonolayers were (b) 0.01, (c) 0.03, and (d) 0.05 ML, respectively. The Ge dots with 0.01 ML C on the wetting layer still showed the hut structure as visible in Fig. 1(b). Meanwhile, the structure of the Ge dots transformed from huts to domes by increasing the thickness of C as shown in Figs. 1(c) and 1(d). Therefore, the essential effect of C on the wetting layer is to enhance the structural

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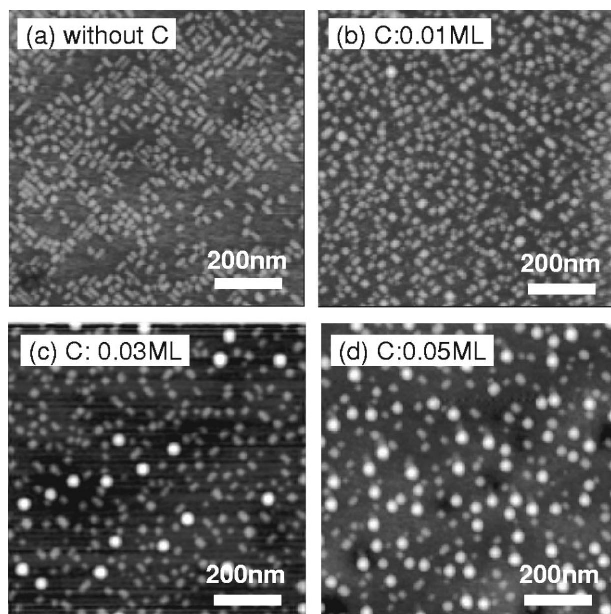

FIG. 1. AFM images of Ge dots with and without submonolayer C on Ge wetting layer. (a) pure Ge 6 Å. The mean thickness of the C layers are (b) 0.01, (c) 0.03, and (d) 0.05 ML.

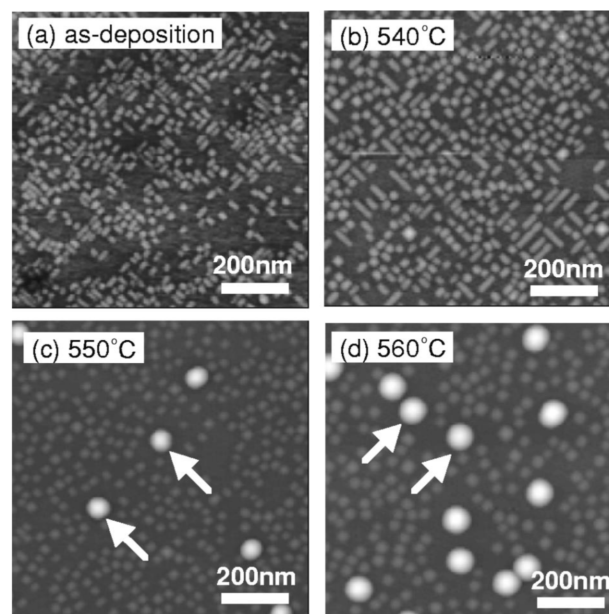

FIG. 2. AFM images of Ge dots with and without postannealing. (a) as-deposited Ge 6 Å [duplicated from Fig. 1(a)]. The temperatures of postannealing are (b) 540, (c) 550, and (d) 560 °C. The domes, indicated by arrows, show quite high size uniformity. For the postannealed samples, the substrate temperature was increased up to each temperature and kept for 5 min followed by cooling down.

transition of the Ge dots from huts to domes. The size of these domes is quite uniform, 40 nm in diameter and 5 nm in height on average.

Carbon induced Ge dot formation has been reported by Schmidt *et al.*[7,8] and Leifeld *et al*.[10,11] They demonstrated remarkable reduction of the Ge dome size by depositing submonolayer C with 0.2 ML in typical thickness on the Si surface. The C atoms diffused into the Si substrate to form a Si–C alloy layer. The surface of Si substrate, as a result, became rough. The reduction of the Ge dome size was attributed to this surface roughness. In short, the surface roughness simultaneously led to a decrease in the surface mobility of the Ge adatoms and an increase in the nucleation probability. For this reason, growth of the Ge domes with small size and high density was achieved.

In contrast, the roughness of the surface induced by alloying between C atoms and the Ge wetting layer is negligible in our cases. This is because that the coverage of the C layers in our experiments is much lower than those in Refs. 7 and 10. In fact, quite clear streak reflection high-energy electron diffraction patterns were observed even after C deposition, which indicated a flat surface. Therefore, the surface mobility of Ge adatoms for the top layer was not affected by the submonolayer C. Consequently, other factors should be taken into consideration to explain the C effect on the structural modification shown in Figs. 1.

In order to explain the C effect, it is important to understand the reason for the coexistence of different Ge dot structures, i.e., huts and domes. For this purpose, Medeiros-Ribeiro *et al.*[12] discussed the configurational energy of the Ge dots by taking account of some energy related parameters, such as a bulk strain, facet and interface energies, and interaction of the facet edges of the Ge dot. They demonstrated that both hut and dome are metastable structures and their configurational energies represent two minima in energy. To initiate a structural transition from huts to domes, a certain activation energy is required.

A slight increase in the substrate temperature effectively induces the structural transition. AFM images are shown in Fig. 2 for the samples of (a) pure Ge deposited at 500 °C and followed by postannealing at (b) 540, (c) 550, and (d) 560 °C. As can be seen, the Ge dots remained in the hut structure up to 540 °C and were gradually transformed to the dome structure above 550 °C. The size was quite uniform particularly with regard to the domes as indicated by arrows in Figs. 2(c) and 2(d). This tendency of the structural transition is similar to those shown in Fig. 1. For the pure Ge dots, postannealing above 550 °C is necessary to overcome the energy barrier between hut and dome structures. These results imply that the effect of the submonolayer C on the wetting layer has a certain similarity to that of postannealing.

Based on these experimental results, it is reasonable to speculate that carbon on the wetting layer has a relevant influence on the configurational energy and, thereby, determines the Ge dot structure. We suppose that, for instance, C atoms terminate the Ge atoms on top of the wetting layer and affect the surface energy. Thus, the interface energy between the wetting layer and the dots may be modified, even though these are homogeneous materials. As a result, the energy barrier between hut and dome and/or configurational energies of these structures are modified. Consequently, carbon on a wetting layer could give rise to the structural transition observed even at 500 °C.

The high uniformity and temperature dependence of the dome size can be explained by a self-limiting mechanism as follows. The compressive lattice strain in the Ge domes increases as the impinging Ge adatoms are incorporated into existing domes. The lattice strain is concentrated in particular around the dome edges.[13] Accordingly, the energy barrier for adatoms to attach to the dome increases with increasing dome size. The growth rate of large domes, thereby, de-

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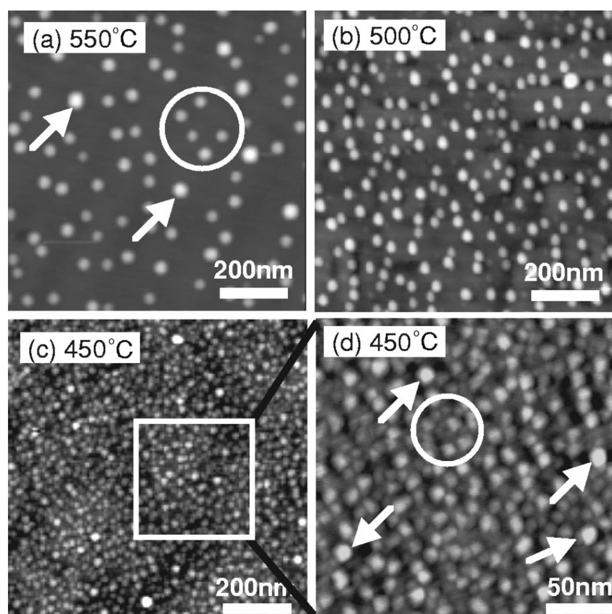

FIG. 3. AFM images of Ge dots deposited at different temperature for top layers. (a) 550, (b) 500, and (c) 450 °C. The wetting layers and submonolayers C were deposited at 500 °C. (d) Enlarged image of Fig. 3(c). Some dots show round shape as indicated by arrows, which are domes. Smaller dots show irregular structure as indicated by a circle, in which no distinct facets and orientation are observed.

creases resulting in the high uniformity of size. As the temperature of the substrate rises, the energy of the adatoms becomes high enough to overcome the barrier to be accommodated into the dome. This is the reason why the size of the dome increases with substrate temperature keeping its high size uniformity. For the same reason, the reduction of the dome size in our experiments is mainly caused by the relatively low temperature of the substrate during deposition. The Ge adatoms cannot overcome the strain energy barrier around the dome, even though its diameter of which is only 40 nm, at the substrate temperature of 500 °C. Thus, the evolution of the domes stops and high size uniformity is obtained at this diameter. The high density of the domes can be attributed to the relatively low mobility of the Ge adatoms at 500 °C.

To get a better insight into the details of the Ge dot structure, the substrate temperature for the Ge top layer deposition was varied, whereas those for the wetting layer and submonolayer C were kept at 500 °C. AFM images in Fig. 3 show Ge dots deposited at (a) 550, (b) 500, and (c) 450 °C, respectively. The mean thickness of submonolayer C is 0.10 ML for all samples.

As the temperature increased, the diameter of the Ge dot increased. The maximum diameter of 550 °C sample is about 60 nm as indicated by arrows in Fig. 3(a). This is comparable to the results obtained from pure Ge deposited at the same temperature (not shown here). These results support our discussion that the main factor to determine the dome size is the substrate temperature but not C on the wetting layer. In this image, the domes show a wide size distribution. Some domes are less than 60 nm in diameter as indicated by a circle, which are on the way of growing.

In a similar manner, the 450 °C sample also shows a wide size distribution ranging from 10 to 20 nm as can be seen in Fig. 3(c) and its enlarged image in Fig. 3(d). In a cross-sectional TEM image shown in Fig. 4(a), a typical dome structure ($\Phi \approx 15$ nm) with the {113} and the {100} facets[4] was observed. On the other hand, some smaller, e.g., $\Phi \leq 10$ nm, islands indicate irregular structures, which are without any clear facets, as shown in Fig. 4(b). These are considered to be the dome structure, the growth of which is still ongoing. Another possibility is that this irregular structure is corresponding to the multifaceted or prism structure described in Ref. 12, which is the intermediate structure between hut and dome. The self-limiting mechanism, which is responsible to the size uniformity of dome, does not work for these dots and results in the wide size distribution. It infers another effect of the submonolayer C, which leads to the modification of the configuration energy of the Ge dots.

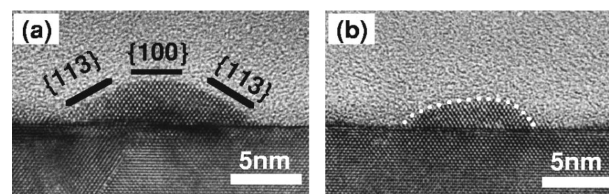

FIG. 4. Cross-sectional TEM images of Fig. 3(c). (a) Dome structure with {113} and {110} facets. (b) Small dots with irregular structure. The deposition temperatures were 500 °C for the wetting layers and C layers and 450 °C for Ge top layer, respectively.

In summary, we investigated the effect of a submonolayer C on the Ge dot structures. The main effect of C is to promote the structural transition from huts to domes. Carbon is supposed to influence the configurational energy to determine the Ge dot structures. As a result, the dome structure was formed even at 500 °C at which only hut structures were formed for the case of pure Ge. The essential experimental parameter to determine the size of the Ge dome is the substrate temperature. Consequently, the combination of two techniques; submonolayer of C on the wetting layer and low-temperature deposition enables us to form small domes with 10–20 nm in diameter.

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