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Modified growth of Ge quantum dots using C_2H_4 mediation by ultra-high vacuum chemical vapor deposition

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ABSTRACT

C_2H_4 mediations were used to modify the Stranski–Krastanow growth mode of Ge dots on Si(0 0 1) at 550 °C by ultra-high vacuum chemical vapor deposition. With appropriate C_2H_4-mediation to modify the Si surface, the elongated Ge hut clusters can be transformed to highly uniform Ge domes with a high Ge composition at the core. These C_2H_4-mediated Ge dots, almost bounded by {1 1 3} facets, have an average diameter and height of 55 and 9 nm, respectively. We propose two major mechanisms to depict the formation of these C_2H_4-mediated Ge dots: (i) an almost hydrogen-passivated Si surface to limit the nucleation sites for dot formation, and (ii) the incorporation of Ge atoms, repelled by the C-rich areas, into the existing Ge dots. This work provides a useful scheme to tune the topography of Ge dots in an UHV/CVD condition for possible optoelectronic applications.

1. Introduction

Recently, the growth of self-assembled Ge quantum dots (QDs) on Si substrates has been intensively investigated for the next generation of Si-based optoelectronic devices [1–3]. Deposition of Ge onto Si(0 0 1) leads to a strain-induced spontaneous formation of the three-dimensional islands as soon as the Ge epilayer exceeds a critical thickness of 3–4 monolayers, which is the well-known Stranski–Krastanow (S–K) growth mode [4,5]. The self-formation of Ge QDs is considered to be energetically favorable since the gain of strain energy due to the partial strain relaxation overcompensates the increased surface energy. However, thermodynamics and kinetics impose certain restrictions on the growth and geometrical dimensions of those Ge QDs. For example, at low growth temperatures, low-adatom mobilities kinetically limit the QDs formation and then result in a thick wetting layer or a broader dot-size distribution within the Ge dot ensemble [6,7]. To circumvent these restrictions, several approaches, such as selective epitaxial growth [8] and thermal annealing [9], have been reported. Recently, Schmidt et al. demonstrated that a very small amount of pre-deposited C onto the Si substrate induces very small Ge dots with enhanced light-output below the critical thickness [10]. However, the size uniformity of those C-induced Ge dots remains a critical issue [11]. It is well known that growth kinetics of the epilayer is controlled by hydrogen desorption in the epitaxial growth front under ultra-high vacuum chemical vapor deposition (UHV/CVD) condition [12]. In the present study, we use ethylene (C_2H_4) mediation to modify the growth mode of Ge dots at relatively low growth temperature in an UHV/CVD system. The results demonstrate that the elongated Ge hut clusters can be transformed to highly uniform Ge domes with a high Ge composition by a modified dot-formation process.

2. Experimental procedures

10–25 Ω cm, 100 mm diameter *p*-type (0 0 1)-oriented Si wafers were used in the present study. All the Ge QDs investigated in this work were grown at 550 °C in a commercially available multi-wafer UHV/CVD system. Pure SiH_4, 2% C_2H_4, and 5% GeH_4 diluted in He were used as precursors. The Si wafers were dipped in a 10% HF solution to achieve the hydrogen-passivated surface, and then transferred into an UHV/CVD system. A 60-nm-thick Si buffer layer was first grown to cover the wafer surface. After depositing

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the Si buffer, Si surface was then pre-mediated by 10-sccm C_2H_4 with different durations prior to Ge dot growth. Subsequently, a 6.8 eq-MLs Ge layer was deposited to form the self-assembled Ge QDs on those C_2H_4-mediated Si surfaces. Note that the amount of Ge deposition is expressed in the unit of equivalent-monolayers (eq-MLs, 1 eq-ML = 6.27×10^{14} Ge atom/cm^2) [13].

The Ge dot shape and size distribution were studied *ex situ* by atomic force microscopy (AFM) in tapping mode. Both plan view and cross-section transmission electron microscopy (XTEM) images were used to provide detailed information about facets and microstructures of the Ge dots. TEM in conjunction with an energy dispersion spectrometer (EDS) was utilized to determine the composition of Ge dots. For the EDS analysis the electron beam can be converged to a size as small as 1.5 nm.

3. Results and discussion

3.1. Topography by atomic force microscopy

Fig. 1 illustrates the topographic evolution of 6.8 eq-MLs Ge dots grown at 550 °C with different C_2H_4-mediated duration. As shown in Fig. 1(a), the Ge dots are predominantly elongated huts accompanying a few pyramid-like islands, which are typically observed at lower growth temperatures. These huts elongated along the two orthogonal ⟨1 1 0⟩ directions were found to have the base width of 10–95 nm with an average height of 2.8 nm. Although with a density up to 1×10^{11} cm^{-2}, these hut islands exhibit the large size fluctuations, which limit their practical applications. However, with C_2H_4 mediation for 15 s, the resulting Ge QDs were found to change their shapes drastically from huts to multi-faceted domes accompanying some superdomes, indicated by arrowheads in the Fig. 1(b). These superdomes may be caused by the agglomerations of neighbor Ge islands, which nucleated simultaneously in a larger C-free region. However, with increasing duration of C_2H_4-mediation to 1 min [Fig. 1(c)], superdomes have vanished completely and multi-faceted domes with a narrow size distribution remained. In addition, the density of these C_2H_4-mediated Ge dots was found to be about 5.4×10^9 cm^{-2}, higher than that corresponding to Fig. 1(b). Those larger C-free regions in Fig. 1(b), with increasing duration of C_2H_4-mediation, are likely to be separated into parts by more C-containing Si surfaces. Consequently, more and smaller C-free regions remain. Therefore, the agglomerations of neighbor Ge islands into superdomes are expected to be suppressed. On the other hand, more nucleation sites for Ge dot formation are provided by those larger C-free regions, resulting in an increase of Ge dot density. However, further C_2H_4-mediation for 10 min [Fig. 1(d)], these C_2H_4-mediated Ge QDs shrunk and island uniformity degraded. In Fig. 2, we summarize the dependence on C_2H_4-mediated duration of both the Ge dot density and size obtained from AFM images. It indicates that, with appropriate C_2H_4-mediation (1 min in this case) to modify the Si surface, the growth of highly uniform Ge QDs with an acceptable dot density can be achieved.

3.2. Microstructures of C_2H_4-mediated Ge QDs

Fig. 3 shows the XTEM images of two typical C_2H_4-mediated Ge dots, which formed in the condition corresponding to that of

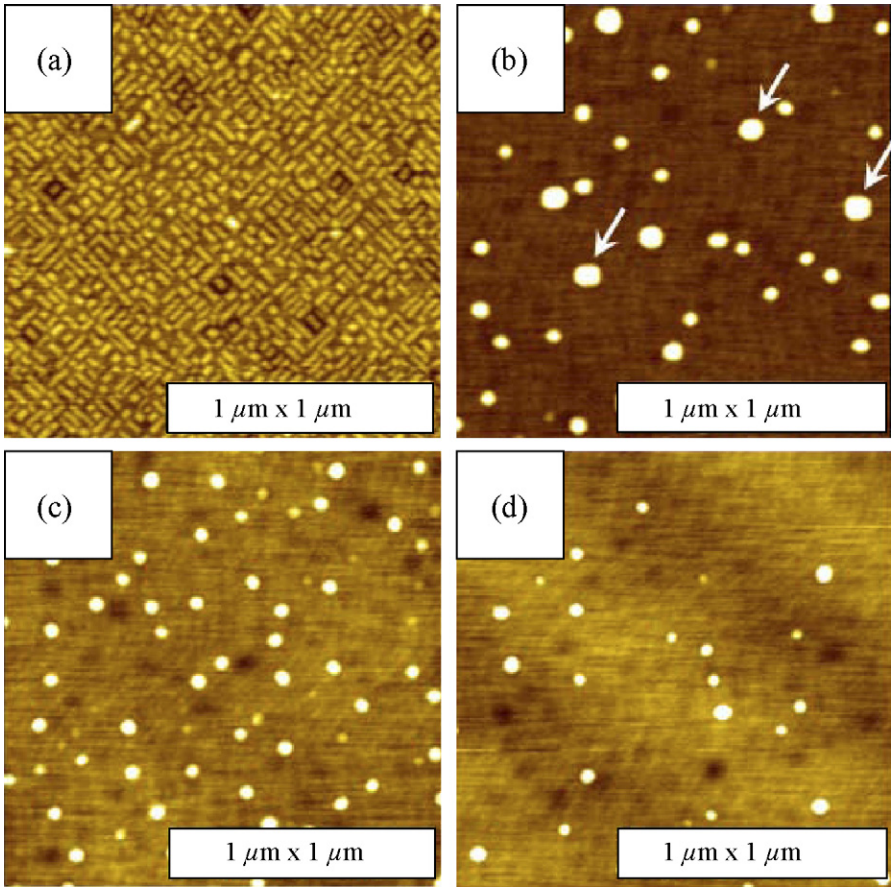

Fig. 1. AFM images (1 μm × 1 μm) of 6.8 eq-MLs Ge QDs on Si(0 0 1) grown at 550 °C (a) without and with the 10-sccm C_2H_4 mediation for (b) 15 s, (c) 1 min, (d) 10 min prior to Ge growth.

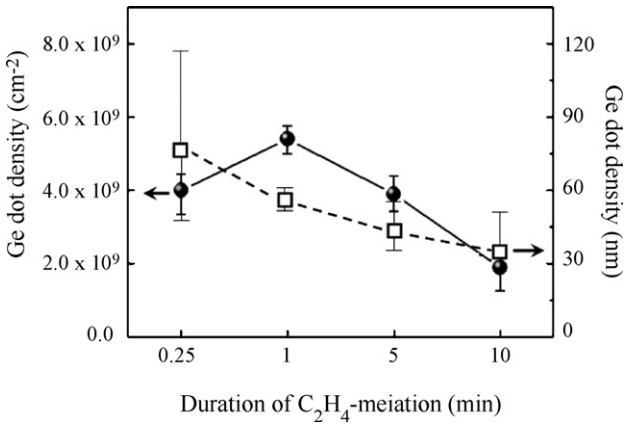

Fig. 2. Dot density and average size of the Ge dots vs the duration of C_2H_4-mediation. Both are obtained from the AFM measurements.

Fig. 1(b) and (c), respectively. As shown in Fig. 3(a), some threading dislocations were found to form in the 15-s-C_2H_4-mediation Ge superdome. It is possibly caused by the simultaneous nucleations and subsequent agglomeration of neighbor Ge islands confined at a limited region. With increasing duration of C_2H_4-mediation to 1 min, no defects such as threading dislocations were observed inside the Ge islands. These defect-free C_2H_4-mediated dots have an average diameter and height of 55 and 9 nm, respectively, yielding an aspect ratio about 3.2 times to that of Ge hut islands. Unlike the larger multi-faceted Ge domes observed at 600 °C in a previous study [14], these C_2H_4-mediated Ge dots are almost bounded by {1 1 3} facets with an inclination of 25.2°, accompanying small {1 0 5} facets with an inclination of 11.3° at the apex. In addition, EDS measurement data indicate that the average Ge composition at the core of C_2H_4-mediated dots is about 83%, much higher than 63% of that of Ge domes grown at 600 °C. These XTEM and AFM observations imply that the original S–K growth mode of Ge islands on Si(0 0 1) has been modified by C_2H_4 mediations prior to Ge growth.

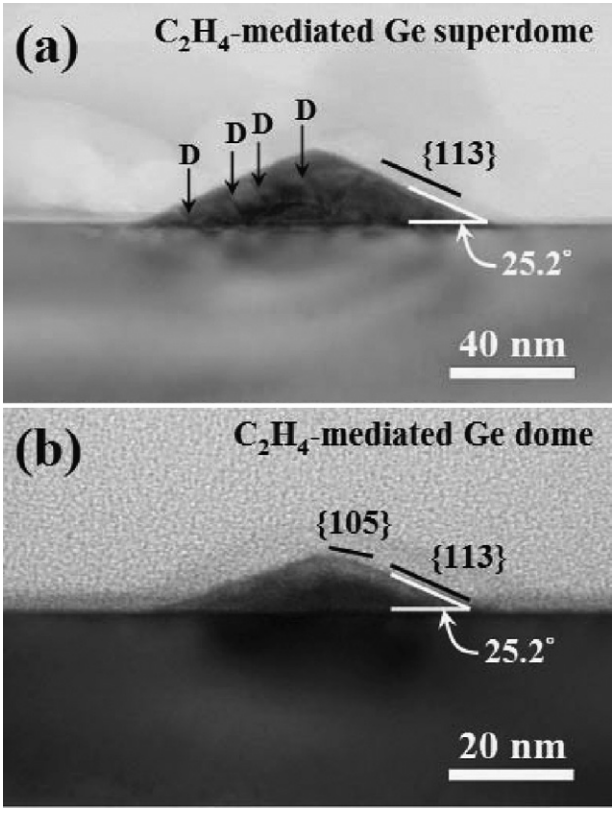

Fig. 3. XTEM images of two typical C_2H_4-mediated Ge dots, which correspond to Fig. 1(b) and (c), respectively. The D marked inside the Ge dot refers to a threading dislocation.

3.3. Mechanism for C_2H_4-mediated dot formation

In this case, due to the stronger C–H bonds than Si–H ones, C_2H_4-mediation prior to Ge growth produces a C-containing Si surface with almost full monohydride coverage [15]. This C-containing Si surface, having a lower rate of hydrogen desorption, leads to a reduction of sticking coefficient of GeH_4 on Si surfaces and then impedes the subsequent deposition of Ge atoms. Therefore, the nucleation sites for the Ge QDs were mostly confined at Si-rich or C-free regions. As can be expected, with the appropriate conditions of pretreatment of Si surface with C_2H_4, the growth of highly uniform Ge QDs can be achieved, as shown in Fig. 1(c).

Considering the much larger volumes of C_2H_4-mediated Ge dots than those of Ge huts, there should be another dot-formation mechanism to supply the increased amount of Ge atoms. It has been reported that the formation of Ge–C bond in the SiGeC material system would involve severe strain because of a difference in bond length as high as ~37% [16]. Therefore, the difficulty to form Ge–C bonds drives the Ge atoms to migrate from the C-enriched surface regions to the existing Ge islands, where the lattice mismatch is the smallest. Consequently, the 3D growth of C_2H_4-mediated islands continues with the incorporation of Ge atoms repelled by the C-rich areas. This assumption is also consistent with our TEM observations that C_2H_4-mediated dots have an extremely high Ge content. Therefore, as illustrated in Fig. 4, two mechanisms can be concluded to depict the formation of C_2H_4-mediated Ge dots: (1) an almost hydrogen-passivated Si surface to limit the nucleation sites for dot formation; (2) the incorporation of Ge atoms, repelled by the C-rich areas, to enlarge the existing Ge QDs.

It is worthwhile to note that the submonolayer C coverage on Si surfaces in the present study plays a different role in the dot formation compared to Schmidt's work [10], in which the pre-deposited C atoms act as nucleation centers for the Ge dot formation. Over the past years, extensive works have been carried out to investigate the surfactant-meditated growth of Ge QDs. For

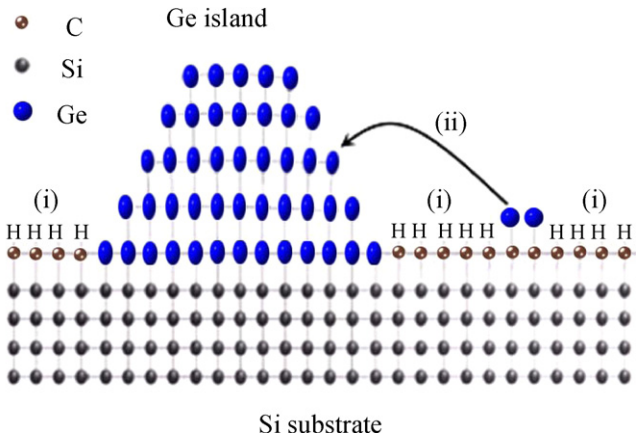

Fig. 4. A schematic view illustrating two mechanisms for the formation of C_2H_4-mediated Ge dots: (i) an almost hydrogen-passivated Si surface and (ii) the repulsive interaction of C and Ge atoms.

Table 1
Comparison of dot-formation mechanisms for the different surfactant-meditated growth of Ge QDs

Authors	Surfactant	System	Dot-formation mechanism
Schmidt et al.[a]	C	SSMBE[d]	C atoms act as nucleation center for dot formation
Portavoce et al.[b]	Sb	SSMBE	Sb atoms suppress the surface diffusion and reduce the dot size
Chen et al.[c]	B	UHVCVD	B atoms weaken H-dangling bonds and provide more nucleation sites
Present study	C	UHVCVD	C atoms limit the nucleation sites for dot formation

[a] Reference [10].
[b] Reference [17].
[c] Reference [18].
[d] Solid-source molecular beam epitaxy.

comparison, the methodologies and their dot-formation mechanisms are summarized in Table 1 The present study, in particular, proposed the mechanism for C_2H_4-mediated Ge dot formation in the UHV/CVD system.

4. Summary and conclusions

In summary, modified growth of self-forming Ge dots on Si(0 0 1) by C_2H_4-mediation at 550 °C was investigated and it was found that growth of self-assembled Ge domes with a narrow size distribution can be achieved with appropriate C_2H_4-mediation to modify the Si surface. Two major mechanisms are proposed to depict this unique growth mode for the formation of C_2H_4-mediated Ge dots: (i) an almost hydrogen-passivated Si surface to limit the nucleation sites for dot formation, and (ii) the incorporation of Ge atoms, repelled by the C-rich areas, into the existing Ge dots. This work provides a useful pathway to tune the topography of the Ge QDs in an UHV/CVD condition for potential optoelectronic applications.

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