Formation of $SiCH_6$-mediated Ge quantum dots with strong field emission properties by ultrahigh vacuum chemical vapor deposition

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Pretreatment of silicon surface with $SiCH_6$ was used to modify the Stranski-Krastanow growth mode of Ge on Si(001) at 550 °C by ultrahigh vacuum chemical vapor deposition. With the appropriate $SiCH_6$ mediation, the elongated Ge hut clusters can be transformed to highly uniform multifaceted domes with a high Ge composition at the core. These $SiCH_6$-mediated Ge dots have an average diameter and height of 38 and 7 nm, respectively. The modified growth mode for the formation of $SiCH_6$-mediated Ge dots can be attributed to (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. The results also demonstrate that $SiCH_6$-mediated dots exhibit the improved field emission characteristics compared to shallow Ge huts. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2060951]

I. INTRODUCTION

The growth of self-assembled Ge quantum dots (QDs) on Si has been intensively investigated for a new generation of electronic and optoelectronic devices in recent years.[1–5] Deposition of Ge on Si(001) leads to a strain-induced spontaneous formation of the three-dimensional (3D) islands as soon as the Ge epilayer exceeds a critical thickness of 3–4 ML, which is the well-known Stranski–Krastanow (SK) growth mode.[6] However, thermodynamics imposes certain restrictions on the growth and geometrical dimensions of those Ge QDs. For example, at low growth temperatures, low adatom mobilities kinetically limit the island formation and then result in a thick wetting layer or a broad island-size distribution within the Ge dot ensemble.[7,8] To circumvent these restrictions, several methods, such as selective epitaxial growth and thermal annealing, have been reported.[9,10] Recently, Schmidt *et al.* demonstrated that the predeposition of a submonolayer of C onto a Si substrate induces very small Ge dots with intense photoluminescence below the critical thickness.[11] However, the size uniformity of those C-induced Ge dots remains an outstanding issue.[12] It is well known that growth kinetics of the epilayer is controlled by hydrogen desorption in the growth front during epitaxy under an ultrahigh vacuum chemical vapor deposition (UHV/CVD) condition.[13] In this work, we use methylsilane ($SiCH_6$) mediation to modify the growth mode of Ge dots at relatively low growth temperature in an UHV/CVD system. The results show that these $SiCH_6$-mediated Ge QDs with a narrow size distribution exhibit the strong field emission characteristics by a modified dot-formation process.

II. EXPERIMENTAL PROCEDURES

10–25 Ω cm, 100 mm diameter *p*-type (001)-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 multiwafer UHV/CVD system. Pure SiH_4, 2% $SiCH_6$, 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 the UHV/CVD system. A 60-nm-thick Si buffer layer was first grown. After depositing the Si buffer, the Si surface was then pretreated by 10 sccm $SiCH_6$ with different durations (i.e., the $SiCH_6$ mediation) prior to Ge growth. Subsequently, a nominal 6.8 eq-MLs Ge layer was deposited to form the self-assembled Ge QDs on those $SiCH_6$-mediated Si substrates. Note that the amount of Ge deposition is expressed in the unit of equivalent-monolayers (eq-MLs, 1 eq-ML $=6.27\times10^{14}$ Ge atom/cm^2).[14]

The Ge dot shape and size distribution were characterized *ex situ* by atomic force microscopy (AFM) in tapping mode. Both planview and cross-section transmission electron microscopy (XTEM) images were used to provide detailed information about the diameter and facets of the Ge nanostructures. TEM in conjunction with an energy dispersion spectrometer (EDS) was utilized to determine the composition of Ge nanostructures. For the EDS analysis the electron beam can be converged to a size as small as 1.5 nm. The electron field emission characteristics were measured under a pressure of 1×10^{-7} Torr in a scanning-probe field emission system. The measurement distances between the anode and emitting surface was fixed at 50 μm.

III. RESULTS AND DISCUSSION

The AFM images in Fig. 1 illustrate the evolution of surface morphology of 6.8 eq-MLs Ge QDs with $SiCH_6$ mediation. The Ge QDs grown at 550 °C are predominantly elongated hut islands terminated by {105} facets, which are typically observed at lower growth temperatures. These huts

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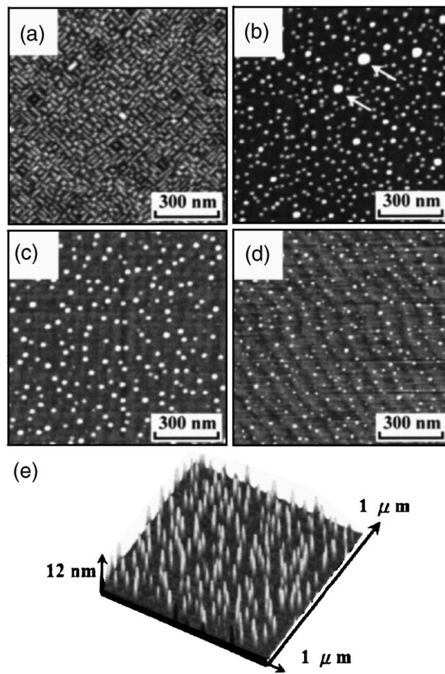

FIG. 1. AFM images (1 μm $\times$ 1 μm) of 6.8 eq-MLs Ge QDs on Si (001) grown at 550 °C (a) without and with the 10 sccm $SiCH_6$ mediation for (b) 5 s, (c) 1 min, and (d) 5 min prior to Ge growth. (e) 3D AFM image corresponding to (c).

were found to have a base width of 10–95 nm with an average height of 2.8 nm. Although with a dot density up to 1×10^{11} cm^{-2}, these hut clusters exhibit the large size and shape fluctuations, which limit their potential applications. With $SiCH_6$ mediation for 5 s, the resulting Ge QDs were found to change their shapes drastically from huts to multifaceted domes accompanying some superdomes, indicated by the arrowheads in Fig. 1(b). With increasing duration of $SiCH_6$ mediation to 1 min [Fig. 1(c)], superdomes have vanished completely and multifaceted domes with a narrow size distribution remained. A 3D image of these $SiCH_6$-mediated dots is shown in Fig. 1(e). An estimation of the broadening of the size distributions for these $SiCH_6$-mediated dots yields a size deviation $\sigma/\langle l \rangle$ ($\langle l \rangle$ is the average size) of $\sim$0.15, which is appreciably smaller than that for the hut clusters ($>$0.8). According to the AFM image, the density of the $SiCH_6$-mediated Ge dots was estimated to be about 4×10^9 cm^{-2}. However, further $SiCH_6$ mediation for 5 min [Fig. 1(d)], the sizes of these $SiCH_6$-mediated Ge QDs were reduced and island homogeneity degraded. The observations indicate that the original SK growth mode of Ge on bare Si(001) has been modified by the $SiCH_6$ mediation prior to Ge growth. In this case, due to the stronger C-H bonds than Si-H ones, the $SiCH_6$ mediation prior to Ge growth produces a C-containing Si(001) 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 accumulation of Ge atoms.[16] Therefore, the nucleation sites for the Ge QDs were mostly located at Si-rich or C-free regions. With the appropriate conditions of $SiCH_6$ mediation to modify the Si surface, the growth of highly

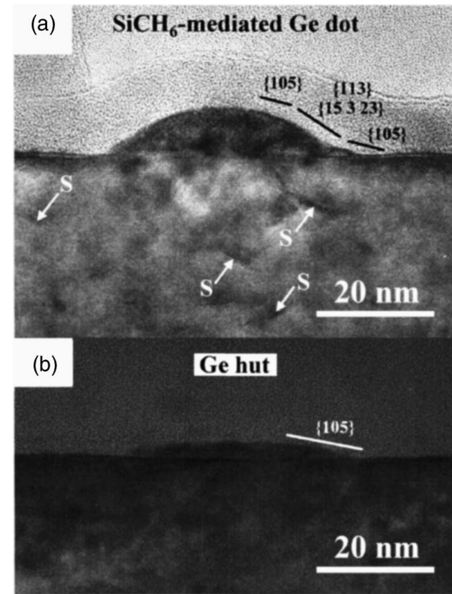

FIG. 2. XTEM images of (a) a typical $SiCH_6$-mediated Ge dot and (b) a Ge hut island, which correspond to Figs. 1(a) and 1(c), respectively. Stacking fault in the buffer layer is marked as S.

uniform Ge QDs was achieved, as shown in Fig. 1(c). One should keep in mind that the submonolayer C coverage on Si surfaces in the present study plays a different role in the dot formation compared to the work of Schmidt *et al.*,[13] in which the pre-grown carbon acts as nucleation centers for the formation of Ge islands in the molecular beam epitaxy process.[11] On the other hand, as described in Sec. I, the growth kinetics of the epilayer is controlled by hydrogen desorption in the growth front under UHV/CVD condition, as in the present instance.

Figure 2(a) shows the XTEM image of a typical $SiCH_6$-mediated Ge dot formed in a condition corresponding to that of Fig. 1(c). Some stacking faults, as marked, were found to form in the Si buffer layer possibly due to the high strain fields underneath the Ge islands. No extended defects such as dislocation were observed inside these Ge islands. These $SiCH_6$-mediated dots have an average diameter and height of 38 and 7 nm, respectively, yielding an aspect ratio about 3.5 times to that of Ge huts, formed prior to the $SiCH_6$ mediation, as shown in the Fig. 2(b). Similar to the larger Ge domes observed at high temperatures, the apex and base of the $SiCH_6$-mediated Ge dots are bounded by {105} facets, whereas the intermediate surface is composed of steeper {113} and {15 3 23} facets. In addition, EDS measurement showed that the Ge compositions at the core of $SiCH_6$-mediated dot is about 76%, higher than 63% of that of Ge domes grown at 600 °C in a previous study.[17]

Considering the much larger volumes of $SiCH_6$-mediated Ge dots than those of Ge huts, an additional dot-formation mechanism has to be operating to supply the increased amount of Ge atoms. It has been reported that the formation of a Ge–C bond in the SiGeC material system would involve severe strain because of a difference in bond length as high as $\sim$37%.[18] 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

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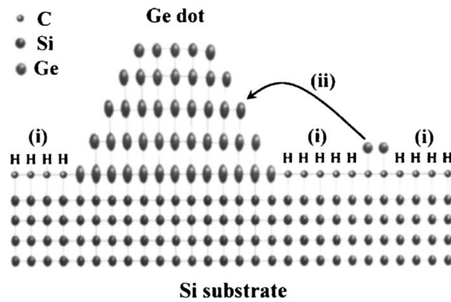

FIG. 3. A scheme illustrating two mechanisms for the formation of $SiCH_6$-mediated Ge QDs: (i) an almost completely hydrogen-passivated Si surface and (ii) the repulsive interaction of Ge and C atoms.

the lattice mismatch is the smallest. Consequently, the 3D growth of $SiCH_6$-mediated dots continues with the incorporation of Ge atoms repelled by the C-rich areas. Therefore, as illustrated in Fig. 3, two mechanisms are proposed to depict the formation of $SiCH_6$-mediated Ge dots: (1) an almost hydrogen-passivated Si surface to limit the nucleation sites for dot formation and (2) the incorporation of Ge atoms, repelled by the C-rich areas, to enlarge the existing Ge QDs.

Figure 4 shows the field emission ($F-E$) characteristics for the $SiCH_6$-mediated Ge dots and huts, respectively. The $F-E$ characteristics were measured repeatedly several times to obtain the stable and reproducible current density-electric field ($J-E$) characteristics. The $SiCH_6$-mediated Ge dots exhibit a turn-on field (defined at a current density of 10 $\mu A/cm^2$) of 12.5 $V/\mu m$, which is much lower than that of Ge huts. It is well known that the turn-on voltage strongly depends on the sharpness of the field emitters.[19] Therefore, the improved turn-on field can be attributed to a higher aspect ratio of the $SiCH_6$-mediated dots compared with the shallow huts. The inset shows the Fowler-Nordheim (FN) plots for the $SiCH_6$-mediated Ge dots. The $\ln(J/E^2)$-$1/E$ plot gives a straight line at a high field, suggesting a FN tunneling process.[20] The field enhancement factor β, which is used to indicate the degree of the field emission enhancement of any tip shape on a planar surface, can be calculated based on the FN equation. The $SiCH_6$-mediated Ge dots were found to possess a β value 300. This result, although yet to be optimized, demonstrates the feasibility of using self-assembled $SiCH_6$-mediated Ge QDs as field emitter arrays. In addition, the $SiCH_6$-mediated Ge QDs field emitter arrays also provide an additional advantage in its compatibility with the current Si-based technology.

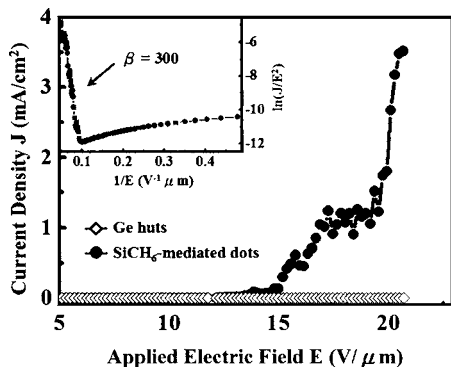

FIG. 4. Plots of field emission current density J (mA/cm^2) against local applied field E ($V/\mu m$) curves for the $SiCH_6$-mediated Ge dots and shallow huts. The inset presents the emission current data plotted with the Fowler–Nordheim relationship for the $SiCH_6$-mediated Ge dots.

IV. SUMMARY AND CONCLUSIONS

In summary, the modified growth of self-assembled Ge dots on Si(001) by $SiCH_6$ mediation at 550 °C have been investigated in this work. With the appropriate $SiCH_6$ mediation to modify the Si surface, the growth of self-assembled multifaceted Ge domes with a narrow distribution can be achieved. This unique growth mode for the formation of $SiCH_6$-mediated Ge dots can be attributed to (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 QDs. The result also demonstrates that $SiCH_6$-mediated dots exhibit much stronger field emission characteristics compared to the shallow Ge huts. The present work provides a useful scheme to utilize self-assembled $SiCH_6$-mediated Ge QDs as field emitter arrays.

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