Nanotechnology **10** (1999) 122–126. Printed in the UK PII: S0957-4484(99)97419-6

# Self-organized growth of Ge quantum dots on Si(001) substrates induced by sub-monolayer C coverages

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Received 10 September 1998

**Abstract.** Ge dots are grown on Si(001) substrates pre-covered with 0.05–0.1 monolayers (ML) of carbon. The C pre-deposition reduces the dot size to less than 20 nm at growth temperatures ranging from 450 to 550 °C. *In situ* scanning tunnelling microscopy (STM) shows that submonolayer C-deposition locally induces c(4 × 4) reconstruction. The reconstruction is assigned to clusters of six C atoms localized in the two topmost atomic layers in between two Si surface dimers. The non-uniform distribution of carbon together with the enhanced surface roughness give rise to the early onset of island formation at Ge coverages as low as 2.5 ML. These islands show intense photoluminescence signals at 4 K. STM and transmission electron microscopy show that the islands are irregularly shaped. No faceting is detected up to coverages of 4 ML. At 5.8 ML of Ge islands with (105) side facets and a (001) top facet are observed.

## 1. Introduction and experimental

Dot structures in the Si/Ge systems are potential candidates for a new generation of electronic and opto-electronic devices. However, the self-formation of Ge hut clusters [1] in solid source molecular beam epitaxy (MBE) leads to rather large dots with diameters not smaller than 50 nm [2, 3]. The growth of small dots by MBE requires low deposition temperatures which typically leads to deteriorated material quality and no significant photoluminescence (PL) has been observed so far. Recently small Ge dots (10 nm) have been fabricated at temperatures as high as 550 °C by MBE using a C pre-deposition procedure [4]. Strong PL has been observed from these C-induced Ge dots, which is explained by the reduced size and the additional electron confinement in a $Si_xC_{1-x}$ well formed underneath the Ge dots [5].

Here we study the effect of sub-monolayer C coverages on Si(001) surfaces. A model of the C configuration at the Si surface and its role in the nucleation of the Ge islands is given. The impact of growth temperature on the structural and optical properties has been studied in detail.

The samples were prepared by MBE in the temperature regime from 350 to 750 °C. Si and Ge were evaporated from e-guns whereas the C was sublimated from a hot C filament. The C sublimation from a hot filament will typically lead to a release of atomic C as well as $C_2$ or $C_3$ clusters. After the deposition of a 200 nm thick Si buffer layer, 0.05–0.11 monolayer (ML) of C and subsequently 2.5–5.8 ML of Ge were deposited. This first layer of dots was capped by 150 nm of Si followed by a second C-induced Ge dot layer. The 4″ sample was then transferred in UHV into the STM chamber [6].

In addition to the STM studies the structural properties were investigated by cross sectional transmission electron microscopy (TEM). Excitation at 488 nm of an $Ar^+$ laser was used for the PL measurements at 4 K. The excitation power was adjusted to 6 mW.

## 2. Results

Figure 1 shows the STM image of a Si(001) surface after depositing 0.11 ML of C. Besides an increase in surface roughness compared with bare Si(001) surfaces, patches of bright double spots are visible, which reveal a c(4 × 4) reconstruction. The inset of figure 1 shows the RHEED pattern giving evidence of the c(4 × 4) reconstruction by the three fractional-order spots observed between the main streaks in the [001]-azimuth. The c(4 × 4) double spots are perfectly aligned with the buckled Si-dimer rows in the same atomic layer. Neighbouring rows are shifted to each other by two lattice constants. The centre of the double spots and the voids between them are always aligned to the middle of the dimer rows in the underlying ML.

After the deposition of only 0.05 ML of C a significant increase in the roughness of step edges on the Si(001) surface

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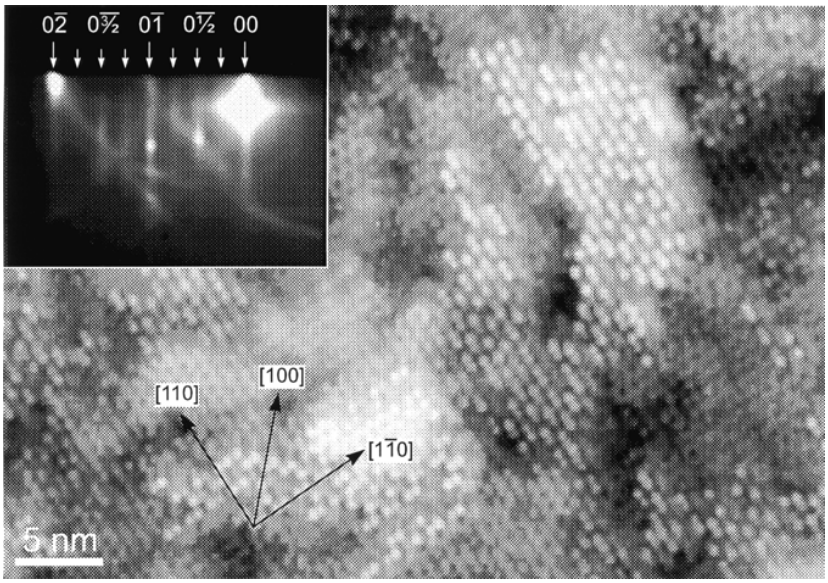


**Figure 1.** STM image of a Si(001) surface covered with 0.1 ML C. Patches of c(4 × 4) reconstruction caused by carbon are observed. Inset: RHEED pattern with three fractional order spots from c(4 × 4) superstructure.

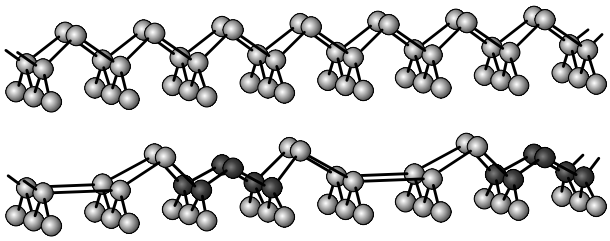

**Figure 2.** Scheme of the atomic arrangement of Si (light grey) and C (dark grey) along [110]. Carbon forms a complex of six atoms in between two Si dimers in each c(4 × 4) surface unit cell. Every third dimer is missing. The paired dimers correspond to the pairs of bright spots in the STM image.

is observed. Both types of step edges, with the dimer rows parallel and perpendicular to the steps, become rough, indicating a large amount of atomic movements on the Si surface which is probably related to the incorporation of C atoms. At these low coverages only a few bright double spots are visible and no distinct patches of areas with c(4 × 4) reconstruction are observed. This suggests that a rather high density of C atoms is required to initiate the c(4 × 4) reconstruction of the Si(001) surface; apparently C atoms on the average in fourth or fifth nearest-neighbour positions are not sufficient to form this reconstruction. Together with the observation that each double spot covers the area of about six Si atoms, i.e. three Si dimers, it is concluded that the double spots contain several C atoms. At C coverages above 0.1 ML the area covered by the c(4 × 4) pattern appears to scale with the amount of C deposited. Comparing the number of double spots per area and the amount of C given by secondary ion mass spectroscopy (SIMS) it is found that each c(4 × 4) unit cell may contain up to 8 C atoms. This is certainly an upper limit since some C atoms may stay on interstitial sites [7] and not every C atom may find enough neighbouring C atoms to initiate the surface reconstruction leading to the double spots in the filled state STM images. Extensive density functional calculations of various arrangements of C atoms in the Si lattice have been performed in order to simulate the observed filled state STM images [8]. Here we only show the structure which gives best agreement between the model calculations and the experimental observations, in addition it is also the energetically most favourable structure. Figure 2 shows a 3D schematic view of this structure containing the three topmost atomic layers along the [110]-azimuth, which is the diagonal of a unit cell. For comparison a simple Si dimer row is also depicted. The atomic configuration leading to a double spot consists of a group of three surface dimers per c(4 × 4) unit cell, formed by two Si dimers and a centre C dimer. The dimers on the right and left of this group, in the corners of the c(4 × 4) unit cell are missing. The C dimer in the middle is backbonded to four additional C atoms in the subsurface atomic layer, yielding six carbon atoms with five C–C bonds. Due to the shorter C–C bond lengths the C dimer is pulled underneath the dimerized Si surface by the underlying C atoms and the two Si dimers are shifted considerably closer towards each other. This could be called a dimerization of Si dimers, or 'meta-dimers'. However, it is rather likely that these C clusters are only stable at the surface and that they will dissolve and move into energetically more favourable positions after they have been overgrown by Si or Ge [9]. But we believe that the C distribution on the surface will be rather non-uniform, exhibiting areas of high and lower C concentrations.

Figure 3 compares Ge dots grown at 550 °C on bare Si surfaces (*a*) and on Si covered with 0.1 ML of C (*b*), (*c*). In addition, the dependence of the root mean square (rms) roughness on the Ge coverage on C pre-covered Si surfaces is shown (*d*). After the deposition of 5.8 ML of Ge on bare Si a low density of (105) faceted Ge 'hut-clusters' with diameters of about 65 nm are observed (*a*). The same experiment but with a C pre-coverage of 0.11 ML leads to a reduction in size to 15–25 nm and a more irregular shape of the pyramids. In addition, these clusters have a (001)

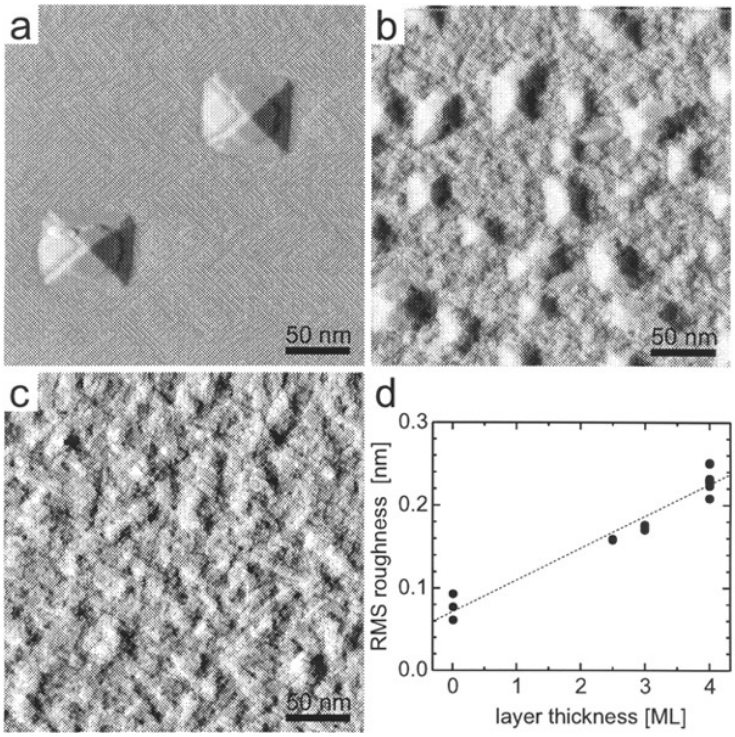


**Figure 3.** STM images of (*a*) 5.8 ML Ge on Si without C pre-deposition, (*b*) 5.8 ML and (*c*) 3 ML Ge on Si with 0.11 ML pre-deposition of C. (*d*) Dependence of rms roughness on Ge thickness grown on C pre-covered Si(001).

facet with missing dimer rows on top, indicating that they still contain a considerable amount of strain. The density of the faceted islands grown on the surface with C pre-deposition is about ten times higher than on bare Si surfaces. For Ge coverages from 2.5 to 4 ML, i.e. below the critical thickness of Ge on bare Si, islands are observed only on the C covered Si surfaces. These dots have a very irregular shape (figure 2(*c*)) and a very high density ($\approx 1 \times 10^{11}$ cm$^{-2}$). Whereas the density remains about constant with increasing Ge thickness, the rms roughness increases (*d*), indicating that the islands grow in height. At a nominal Ge coverage of 3ML, for instance, the growth front already involves at least nine atomic layers, deduced from STM images. The presence of C atoms on lattice sites within the Si surface, i.e. the presence of the c$(4 \times 4)$ reconstructed C patches on the Si surface appears to be essential for the nucleation of these Ge dots. Certainly the non-uniform distribution of C will lead to an undulating strain field at the surface which may play a dominant role in the early onset of Ge islanding.

For further information on the growth mechanisms of this new type of C-induced Ge dots the effect of the deposition temperature on the dot formation was investigated. Figure 4 depicts four cross sectional TEM images taken from samples with 0.11 ML C and 2.5 ML Ge grown at (*a*) 350 °C, (*b*) 550 °C, (*c*) 650 °C and (*d*) 750 °C. Ge dots are only found at temperatures of 450 and 550 °C. At 350 °C a defective two-dimensional quantum well layer is observed (dark line in figure 4(*a*)) and no dots are formed. This is most likely due to the limited surface mobility of the C and Ge atoms at this low temperature. At 650 °C on the other hand a smooth well is observed. In this case the pre-deposited C smears out into the surrounding material and dots do not form. At 750 °C SiC precipitates are formed (dark spots in figure 4(*d*)).

The photoluminescence (PL) data obtained from these samples are in agreement with the structural information from TEM. As shown in figure 5, at 650 and 750 °C only the TO-phonon line of Si close to 1.1 eV is visible. Besides this line, defect related broad-band luminescence is observed for the sample grown at 350 °C. Photoluminescence which is related to the deposition of the C-induced Ge quantum structures is only observed at growth temperatures of 450 and 550 °C as indicated by a doublet with one peak at 1.089 eV and the second peak at 1.036 eV. At 450 °C the spectrum is slightly broadened compared with the PL spectrum of the sample grown at 550 °C. Since the energetic distance of 53 meV matches well with the expected phonon energy, we attribute these two peaks as a no-phonon (NP) line and the corresponding TO-phonon line. These lines can either be attributed to the wetting layer, which may contain C and Ge interdiffused with Si or to the C-induced Ge dots. For a two-dimensional system like the wetting layer, a well-resolved spectrum with rather narrow lines is expected; moreover, the TO-phonon line typically has an intensity comparable to the NP line for quantum wells in the Si–Ge–C material system [10]. In the obtained PL spectra the rather well-resolved separation of the TO-phonon and NP line would suggest a two-dimensional confinement, whereas the weak intensity of the TO-phonon line suggests luminescence of low-dimensional structures in Si [11]. At this point we would like to stress that the amount of C and Ge is rather small, 0.11 and 2.5 ML, respectively. At these coverages the onset of island formation is observed. At a higher C coverage (0.2 ML) the formation of the C-induced Ge

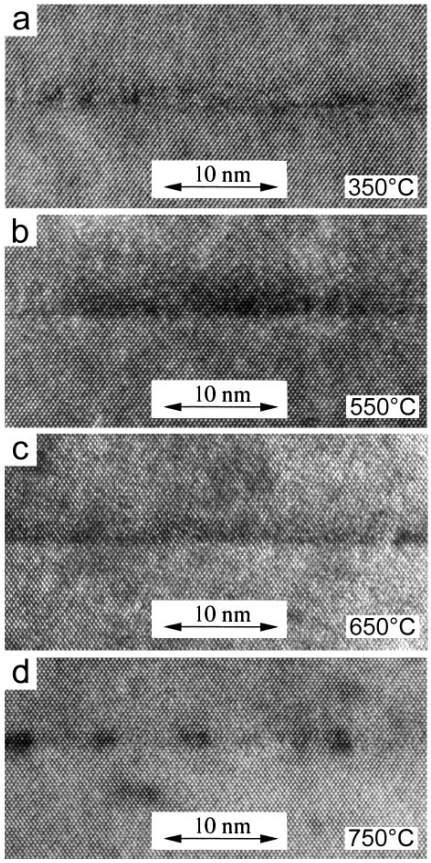


**Figure 4.** TEM cross section of dot structures (0.11 ML C, 2.5 ML Ge) grown at different temperatures: (*a*) 350 °C, (*b*) 550 °C, (*c*) 650 °C and (*d*) 750 °C.

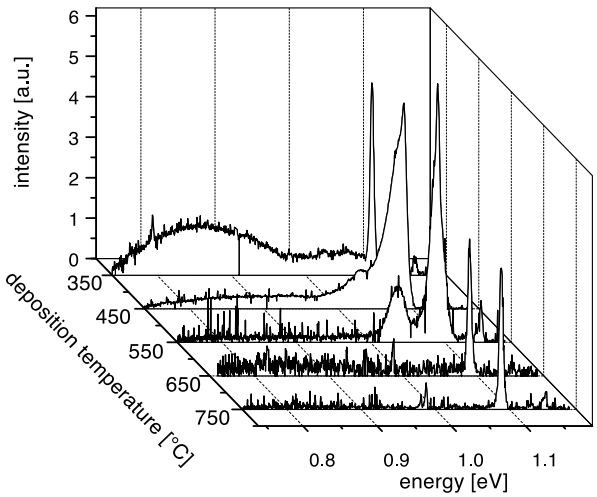


**Figure 5.** 4 K PL spectra of C-induced Ge dot structures grown on Si(001) surfaces at temperatures ranging from 350 to 750 °C. All samples contain 0.11 ML C and 2.5 ML Ge.

dots is obtained at an even smaller number of Ge ML [4], indicated by PL lines assigned to dots at a Ge coverage of 2.16 ML.

The observed PL most likely originates from the areas where the islands are found that consist of stacks of 5–7 terraced ML of Ge. This system can also be considered as

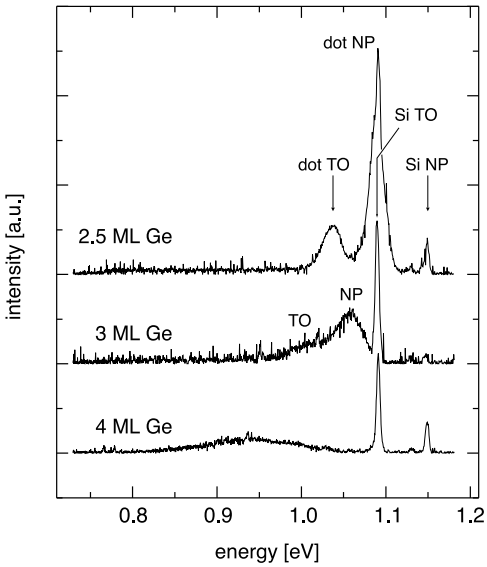


**Figure 6.** 4 K PL spectra of C-induced Ge dot structures on Si(001) grown at 550 °C. The C pre-deposition is kept at 0.11 ML and the Ge thickness is varied between 2.5 ML and 4 ML.

a very rough wetting layer with large thickness fluctuations. Due to the high density of the islands, i.e. areas of wide 'well width', it is expected that the excited carriers are collected very efficiently in these areas with the lowest states in energy. The energy at 1.08 eV is rather high for luminescence from Ge islands, however one has to consider that the strain of Ge towards Si is partly compensated by the C, which will lead to an increase of the band gap of these islands compared with islands formed in the Si–Ge system. In addition, the TEM reveals a very narrow wetting layer of only 1–2 ML between the dots. This SiGeC wetting layer is expected to give PL at even higher energies.

In figure 6 PL spectra of three samples are shown containing C-induced Ge dots embedded in Si. The amount of C was kept constant at 0.11 ML whereas the Ge thickness was varied from 2.5 to 4 ML. The PL peak shifts from 1089 meV at 2.5 ML, to 1060 meV at 3 ML and to a broad peak centred around 940 meV at 4 ML. This large shift of 149 meV in energy is a strong indication for the PL of islands, since the thickness increase of 1.5 ML of a two-dimensional quantum well would lead to a much smaller energy shift of only 66 meV $ML^{-1}$ according to [12] for a pure Ge wetting layer. The broadening of the PL spectra with increasing amounts of Ge deposited indicate that the size distribution of the islands becomes wider.

For a more exact interpretation of the PL mechanisms it would be important to know whether the Ge islands grow on top of the C patches or in between them. In the first case the enhancement in PL intensity in comparison to two-dimensional SiGe quantum well structures can be explained by a spatially indirect type II recombination within the C-induced Ge islands [4]. In the latter case enhanced confinement effects may be the origin for the intense PL. At this stage it remains unclear whether the islands form on top of the C rich areas or in areas in between them. On the one hand Ge–C bonds are even less favourable than Si–C bonds which may lead to an accumulation of Ge in areas with no or low C

concentrations. On the other hand SiC alloys have a smaller and SiGe alloys a bigger lattice constant than Si. Therefore the accumulation of Ge on top of the C rich areas would lead to a strain compensation, which might be favourable. Some initial TEM data suggest that the Ge grows on top of the C patches, but further studies are required to establish this first indication.

## 3. Conclusion

We studied the impact of pre-deposited C on the formation of Ge dots on Si(001) surfaces. It was shown that the deposition of 0.05–0.11 ML of C induces locally c($4 \times 4$) reconstructed areas with C dimers at the Si surface. An atomic model to explain the STM images was proposed involving a complex of six C atoms positioned between two Si dimers. The results imply that the strain fields related to the c($4 \times 4$) reconstructed areas lead to a high density ($1 \times 10^{11}$ cm$^{-2}$) Ge dot formation at Ge coverages well below the critical thickness of Ge on Si. These Ge dots are not faceted but have an irregular shape. At a Ge thickness exceeding the critical thickness for Ge on bare Si, Ge dots with (105) facets occur ('hut-cluster'). The density on surfaces pre-covered with 0.11 ML of C is ten times higher than of the hut clusters grown on clean Si. The C-induced Ge dots are optically active and strong PL was observed at 4 K for Ge coverages in the range 2–3 ML.

## Acknowledgment

Part of this work was financed by the Swiss National Foundation, project No SNF 2129-5 434.95.

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