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# Nanometer-scale Si selective growth on Ga-adsorbed voids in ultrathin SiO<sub>2</sub> films

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### Abstract

We examined nanometer-scale Ga selective doping by Si growth on Ga-adsorbed voids in ultrathin silicon-dioxide on Si(111) surfaces. The doping processes were observed by scanning tunneling microscopy (STM). Voids in ultrathin oxide films were plugged with a  $(\sqrt{3} \times \sqrt{3})$ -Ga structure, and the selective growth was performed by introducing disilane gas (Si<sub>2</sub>H<sub>6</sub>). Si crystals were selectively grown only in the voids at 460–550°C. Two-dimensional nucleation was found to start from the edge of the voids. Incorporated Ga atoms mostly segregated during the selective growth and were reconstructed to the  $(\sqrt{3} \times \sqrt{3})$  structure by annealing at 600°C. These results show that Ga doped dots of nanometer-scale can be formed by selective epitaxial growth using an ultrathin silicon-dioxide mask. © 1999 Elsevier Science B.V. All rights reserved.

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Selective growth of nanometer-scale is an important technique for nanofabrication. Fujita et al. have previously reported nanometer-scale Si selective growth using voids in an ultrathin silicondioxide (SiO<sub>2</sub>) film [1]. They formed the ultrathin SiO<sub>2</sub> film on the Si(001) surface by thermal oxidation and the windows of nanometer-scale were opened by thermal decomposition of oxide film. Then Si crystals were selectively grown in the windows. This technique of utilizing the voids in the ultrathin  $SiO_2$  film can be applied for fabricating nanometer-scale dot structures. If the dopant is incorporated into the Si crystals selectively grown in the voids, the doping dots of nanometer-scale can be formed.

In this letter, we describe nanometer-scale Si selective growth in Ga-adsorbed voids on the Si(111) surface. The Si(111) surface was selected because the reconstructed structure of Ga-adsorbed surface on Si(111) is simple compared with that of the Si(001) surface [2,3], and is suitable for investigating the growth mode. Ga-adsorbed Si(111) surfaces have two main

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structures: a  $(\sqrt{3} \times \sqrt{3})$ -Ga structure for a 1/3 monolayer (ML) of Ga [4] and a  $(6.3 \times 6.3)$ -Ga structure for a 1 ML of Ga [5,6]. The Si(111) surface is easily uniformly covered with one domain of Ga induced structure if the coverage is adequately controlled. In our case Ga atoms are adsorbed in the voids which are formed by thermal decomposition of the oxide. Therefore the surface structures are more complicated due to the diffusion and desorption of Ga atoms on the oxide. The reconstructed surfaces of Ga-adsorbed voids were investigated, and the two structures mentioned above were observed depending on the annealing conditions. Disilane gas was supplied to these Ga-adsorbed voids, and Si selective growth was achieved in the voids of the  $(\sqrt{3} \times \sqrt{3})$ -Ga structure. In the previous work, Si epitaxial growth on wide Si(111)-( $\sqrt{3} \times \sqrt{3}$ )-Ga terraces was reported [7]. However, the growth on the narrow areas of the  $(\sqrt{3} \times \sqrt{3})$ -Ga structure has not yet been clarified. Hence we discuss the Si selective epitaxial growth in the voids of Si(111)-()-Ga surface. The processes during the void formation, Ga adsorption, and selective epitaxial growth were observed by scanning tunneling microscopy (STM).

The samples were cut from n-type well-oriented Si(111) wafer, whose misorientation was  $< 0.5^{\circ}$ . After cleaning the sample, an ultrathin silicondioxide film with a thickness of 0.3 nm was produced in the same way as previously reported [1]. The voids were formed during the thermal decomposition of the oxide films at 720°C. During annealing the sample, voids started to appear randomly on the oxide surface. The density of the voids increased and they extended isotropically with increasing annealing time [8]. When the diameter of voids reached 5-20 nm, the sample was quenched to stop further extension of the voids. The bottoms of the voids were flat and were composed of Si(111)-(5  $\times$  5) and Si(111)-(7  $\times$  7) reconstructions. A 1/3 ML of Ga  $(2.6 \times$  $10^{14}$  cm<sup>-2</sup>) was deposited at 550°C and the sample was annealed to form a stable structure of Gaadsorbed voids. Then Si was selectively grown by introducing disilane gas  $(Si_2H_6)$  at 460–550°C. The dose rate of disilane gas was fixed at  $2 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}$ . Through these processes, STM topographic images of the surfaces were acquired with the constant current between 0.06 and 0.1 nA. Most images were obtained at sample biases of 4–5 V because of the large band gap of SiO<sub>2</sub> [9,10], but lower biases of 2–3 V were applied to the sample when the Si surface or Ga-adsorbed surface structures were observed.

After adsorption of a 1/3 ML of Ga at 550°C, a  $(6.3 \times 6.3)$ -Ga patchwork pattern was observed in the voids. In this stage some amount of Ga was thought to be adsorbed on the oxide, because the image was sometimes disturbed by protrusions with the diameter of > 10 nm which seemed to be Ga droplets. Since Ga atoms on the oxide seemed to flow into the voids, effective coverage in the voids increased to >1/3 ML and the surface of the voids showed the  $(6.3 \times 6.3)$ -Ga structure. Disilane gas (Si<sub>2</sub>H<sub>6</sub>) was introduced to these  $(6.3 \times 6.3)$ -Ga voids at 450°C, and the void surface was observed during gas supply. But the surface structure of patchwork pattern showed no change for 26 min. The growth rate of Si crystals in the  $(6.3 \times 6.3)$ -Ga was estimated to be  $< 0.1 \text{ ML h}^{-1}$ and was not practical for selective growth. This is due to the strong passivation effect of the  $(6.3 \times 6.3)$ -Ga structure.

In order to decrease the Ga coverage on the oxide film and to form a  $(\sqrt{3} \times \sqrt{3})$ -Ga structure, the sample was annealed at  $>600^{\circ}$ C. Fig. 1a shows the images of Ga-adsorbed voids after annealing at 650°C for 2 min. A straight line in this image corresponds to an atomic step, and the height difference between the oxidized Si(111) terraces is a multiple of that of the silicon bilayers (0.31 nm). In the terraces there are the Ga-adsorbed voids with the diameter of 5-20 nm. The surfaces of the voids are flat and there are no  $(6.3 \times 6.3)$ -Ga structures. The protrusions of the Ga droplets on the oxide surface were considerably decreased. These results shows that the evaporation of excess Ga on the voids and the oxide caused the  $(6.3 \times 6.3)$ -Ga structure to disappear and a flat  $(\sqrt{3} \times \sqrt{3})$ -Ga structure remained in the voids. In recent work, Ga atoms on the oxide prove to be easier to desorb than on Si surface [11]. Therefore most Ga atoms on the oxide and some portion of



Fig. 1. (a) STM image of voids, Ga-adsorbed at 550°C and annealed at 650°C. (b) Magnified STM image of the void.  $(\sqrt{3} \times \sqrt{3})$ -Ga reconstruction is observed in the voids.

Ga atoms in the  $(6.3 \times 6.3)$ -Ga voids seemed to desorb by the annealing. Fig. 1b shows the magnified image of Ga-adsorbed void. The void with the diameter of ca 10 nm is plugged with a  $(\sqrt{3} \times \sqrt{3})$ -Ga structure in whole. Most of the edges of the Ga-adsorbed areas are seen to be parallel to the  $\langle \bar{1}\bar{1}2 \rangle$  direction because of its tendency to align in this direction. This  $(\sqrt{3} \times \sqrt{3})$ -Ga structures in the voids did not change after repeated annealing at 650°C for a few minutes. It is known that the number of Ga atoms on a Si(111) surface decreases exponentially with the annealing time [12]. According to this exponential law, Si(111)-(7 × 7) structures are expected to appear gradually with increasing annealing time. However, in our experiment, small amount of Ga atoms remained on the oxide and they are supplied to the voids to form the stable ( $\sqrt{3} \times \sqrt{3}$ )-Ga structure. In fact, once the voids of Si(111)-(7 × 7) structure appeared after repeated annealing, the number of the voids was rapidly increased with annealing time. Because there were no Ga atoms on the oxide and the ( $\sqrt{3} \times \sqrt{3}$ )-Ga structure could not be formed in the voids.

After forming the voids of the  $(\sqrt{3} \times \sqrt{3})$ -Ga structure, disilane gas was introduced to the sample in the growth temperature range of 460-550°C. Fig. 2 shows sequential images of Si selective epitaxial growth on the Si(111)-( $\sqrt{3} \times \sqrt{3}$ )-Ga void surface at 490°C. The images were taken (Fig. 2a) before, (Fig. 2b) 15 min after, and (Fig. 2c) 56 min after the Si growth had started. In Fig. 2a, all the voids were composed of the flat structures before the growth and the  $(\sqrt{3} \times \sqrt{3})$ -Ga structures were observed at higher magnification. In Fig. 2b, the growth starts from the edge of the voids and the islands were grown in a layer-by-layer fashion. Step edges of the growth are parallel to the  $\langle 1\bar{1}0 \rangle$ direction. It is reported that typical two-dimensional nucleation takes place only in the middle of the terraces in the Si epitaxial growth on the Si(111)-( $\sqrt{3} \times \sqrt{3}$ )-Ga surface using disilane gas [7]. In our case, however, the area in which the Si growth is allowed to proceed is likely to be smaller than the diffusion length of Si hydride dissociated from disilane molecules on the Si(111)- $\sqrt{3}$ -Ga surface. Although there are some point defects in the middle of the void as shown in Fig. 1b, there may be more defective regions at the edge of the void where Ga coverage is not perfect. These regions are likely to be nucleation sites. Therefore Si hydride is supposed to migrate in the void and to be trapped at the edge. Ga-adsorbed voids are covered with one bilayer of Si after ca 50 min, and the second layer starts to grow at smaller voids in Fig. 2c. It is expected that the nucleation rate is proportional to the circumference, that is,  $\propto \sqrt{A}$ , where A is the area of the voids and the layer-by-



Fig. 2. Sequential STM images of selective epitaxial growth on Ga-adsorbed voids on Si(111) at 490°C. The dose rate of disilane is  $2 \times 10^{14} \text{ s}^{-1} \text{cm}^{-2}$ . Images were acquired: (a) before; (b) 16 min after; and (c) 56 min after the start of growth.

layer growth rate in the depth direction is proportional to the reciprocal of areas (1/A). Therefore the total growth rate is roughly proportional to  $1/\sqrt{A}$  and the second layer is thought to grow faster at the smaller voids.

To investigate the effect of Ga in the voids, the selective growth in the voids with and without Ga were examined at 550°C. In the case without Ga, the growth proceeded in a layer-by-layer fashion like the case with Ga. But the nucleation occurred both at the edges and in the middle of the voids and the growth rate of Si was ca 2.5 times higher than that in Ga-adsorbed voids because Si dangling bonds were not terminated.

After the growth in the voids of the (Si(111))- $\sqrt{3}$ -Ga structure, the surface was found to be flat but no reconstruction was observed. Most of the Ga atoms were expected to segregate on the surface, but the growth temperature was not high enough for the reconstruction [13]. Then the sample was annealed at 600°C in order to confirm the existence of Ga atoms. Fig. 3 shows the void surface after selective growth at 550°C and subsequent annealing at 600°C. About five bilayers of Si were grown only in the voids after 183 min. In Fig. 3a, some islands are seen to be much higher than those in other voids. This may be due to Ga atom diffusion in these voids to the outside of the voids during the growth. The growth rate was accelerated, since the Ga atoms on the Si(111) surface are known to reduce the dissociation of disilane. In Fig. 3b, the grown island is almost isotropic though there are a few bunched steps at the sidewall of the island. In this image the top surface of the island shows a  $(\sqrt{3} \times \sqrt{3})$  structure. It is likely that some portion of Ga atoms were incorporated in the Si layer but most of them segregated during the growth and were reconstructed on the top surface by annealing. The temperature dependence of the Ga-incorporation coefficient has been previously reported [14]. By extrapolating the relationship, the Ga concentration incorporated in the grown layer at 460-550°C is estimated to be  $2-5 \times 10^{18}$  cm<sup>-3</sup>. This concentration means that a few Ga atoms are incorporated in the central Si island shown in Fig. 3b. If the higher concentration is required, the growth temperature must be lowered.

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Fig. 3. (a) STM image after selective growth at 550°C and subsequent annealing at 600°C. About five bilayers of Si have selectively grown in the voids. (b) The magnified image of growth area identified by the arrow in (a). A  $(\sqrt{3} \times \sqrt{3})$ -Ga reconstruction is observed on the grown area.

In summary, Si selective growth on Gaadsorbed voids was performed on Si(111) surfaces by using disilane gas. The  $(\sqrt{3} \times \sqrt{3})$  structure was formed in the voids with diameters of 5–20 nm after suitable annealing conditions. Si was selectively grown only in voids in a layer-by-layer fashion and nucleation starts from the edge of the voids. Ga atoms partly incorporated during the selective growth are likely to segregate to the top surface. These results show that Ga-doped dots can be formed by selective epitaxial growth by using an ultrathin silicon-dioxide mask.

Nanometer-scale windows have recently been fabricated by a focused electron beam [15] or a field-emission electron beam from an STM tip [16,17]. If dopant-adsorbed voids are formed by these techniques, nanometer-scale dots and wires can also be formed at predetermined areas.

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