Periodic alignment of Si quantum dots on hafnium oxide coated single wall carbon nanotubes

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We demonstrate a bottom up approach for the aligned epitaxial growth of Si quantum dots (QDs) on one-dimensional (1D) hafnium oxide (HfO_2) ridges created by the growth of HfO_2 thin film on single wall carbon nanotubes. This growth process creates a high strain 1D ridge on the HfO_2 film, which favors the formation of Si seeds over the surrounding flat HfO_2 area. Periodic alignment of Si QDs on the 1D HfO_2 ridge was observed, which can be controlled by varying different growth conditions, such as growth temperature, growth time, and disilane flow rate. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3103547]

Si quantum dots (QDs) are utilized for a wide range of applications including traditional electronics such as memory,[1,2] optoelectronics,[3,4] and biotechnology.[5] Single QD devices have been fabricated to outperform current devices such as field effect transistors[6] for ultralarge scale integration. Several options are already available via top-down approaches such as electron beam lithography and nanostamping[7] that can fabricate single QD devices. Another popular method is the growth of QDs via self-assembly instead of fabrication. One of the major hurdles in this approach is the alignment of the QDs themselves. Here we demonstrate a solution to Si QD alignment using a HfO_2 covered single wall carbon nanotube (SWCNT) template.

The template comprises of HfO_2 ridges formed by atomic layer deposition growth of a HfO_2 thin film on SWCNTs on a silicon dioxide (SiO_2) surface. The major advantage for the use of SWCNTs is in their one-dimensional (1D) shape and nanometer scale diameter, which will enable applications to go beyond the complementary metal-oxide-semiconductor (CMOS) ultimate limit. The technique of selective area epitaxy[8,9] has reported the alignment of QDs on Si ridges. This technique starts with a top-down patterned template, followed by a bottom up growth of QDs. This process requires a smooth surface so that during the QD growth the adatoms can migrate to the lowest energy spots. Traditionally, single crystal surfaces have been used for the alignment of QDs via selective epitaxial growth or QD superlattice growth. The atomic layer deposition technique can produce HfO_2 thin dielectric films with smooth conformal polycrystalline surfaces, which can be used for QD self-assembly.[10] QDs grown on HfO_2 surfaces may have potential applications in nonvolatile nanocrystal memories.

The experimental procedure is as follows. SWCNTs were grown on SiO_2/Si substrates using a chemical vapor deposition technique.[11,12] The nanotube samples were then subjected to an UV cleaning for 5 min to make the substrate surface hydrophilic. This time was adjusted to ensure good precursor adhesion as well as keeping the CNTs intact. Following the surface treatment procedure, the samples were introduced to a Cambridge Nanotech Savannah 100 atomic layer deposition chamber. The system ran at a partial pressure of 3×10^{-1} torr and a deposition time of 5 s was used for both precursor and source. Substrate temperature for the HfO_2 deposition was kept constant at 250 °C. The Si QD deposition was done in a custom built gas source molecular beam epitaxy system. The disilane (Si_2H_6) source points directly at the substrate. The base pressure was in the order of 10^{-8} torr, while growth pressure was in the range of 10^{-5} torr. The samples were heated via a Ta heating coil that coupled with the sample holder. Temperature readings were taken by a thermocouple situated between the sample and the heating coil. The source gas flow was controlled using a mass flow controller UFC 1660. Atomic force microscopy (AFM) characterization was carried out using a Veeco multimode AFM.

Figure 1(a) shows a schematic of aligned Si QDs on HfO_2 covered CNTs formed by selective epitaxial growth. The QDs are drawn only on the 1D HfO_2 ridge created by the underlying CNTs. Other QDs could be formed on the surrounding flat surface depending on the magnitude of the length of Si adatom migration on HfO_2 and the proximity of adjacent CNTs. Figure 1(b) shows a cross-sectional SEM image of a QD alignment sample. The HfO_2 thickness is 6 nm and the ridge height was measured to be 1–1.2 nm by AFM characterization. QDs are clearly observed to align along the 1D HfO_2 ridge, while QDs are also seen on the flat surface close to the CNT ridge. The QDs on top of the CNT are larger in size demonstrating that more Si adatoms preferentially migrated to the 1D ridge. We hypothesized that if the density of CNTs is increased, selective growth of Si dots only on the ridges will be evident. The HfO_2 layer is highly conformal on the SiO_2 surface as the shape of the CNT is seen in the SEM image. The CNT surface however is not chemically active[13] so fewer layers are deposited over the ridge than the rest of the film. This characteristic can be advantageous in a circuit setting by utilizing different thicknesses of the oxide film in between CNT channels[14] as the local oxidation of silicon equivalent of isolating oxide.

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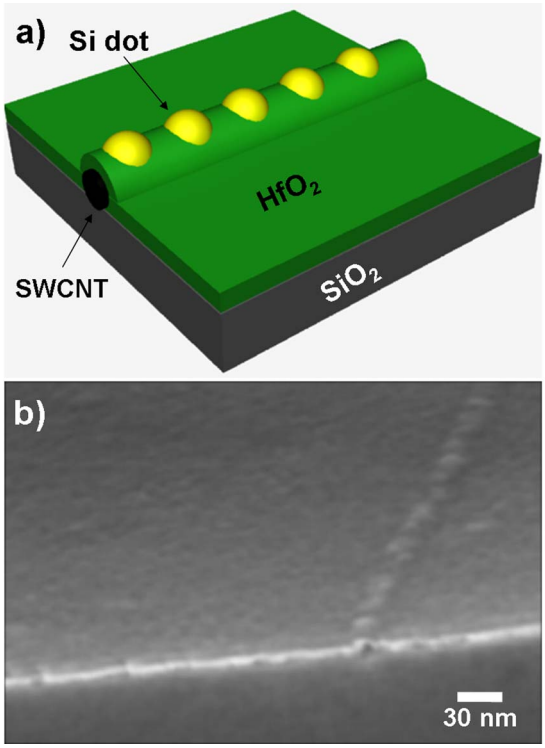

FIG. 1. (Color online) QDs on a hafnium oxide covered CNT. (a) Schematic of a cross-sectional view of the structure. (b) SEM image cross sectional shows aligned QDs on a HfO_2 covered CNT.

To ensure that the observed QDs on the surface are Si dots rather than HfO_2 grains due to annealing, an experiment comparing the annealed samples before and after disilane flow was introduced. Figures 2(a) and 2(b) show the AFM images of these samples. Both samples began with the 6 nm HfO_2 covered CNT. The *in situ* annealing including ramping from room temperature to 650 °C within 2 h and maintaining at this temperature for 8 min was used for both samples. The control sample which was not subjected to disilane growth shows relatively smooth surface, while the sample with disilane flow of 1.6 SCCM (SCCM denotes standard cubic centimeter per minute at STP) for 8 min shows rough surface with QD alignment.

The growth processes of the selective area epitaxy can be observed clearly through the changes in QD linear density. The QD linear density was obtained via AFM measurement along the CNT ridge. Figures 3(a)–3(d) show the morphology of the samples grown at different flow rates. A higher rate of disilane flow results in smaller and denser

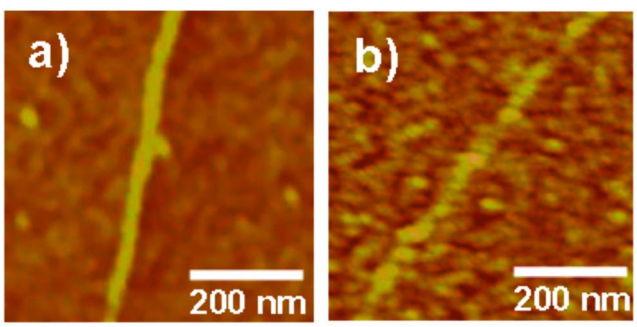

FIG. 2. (Color online) AFM images of HfO_2 covered CNT after *in situ* annealing, (a) before and (b) after the introduction of disilane.

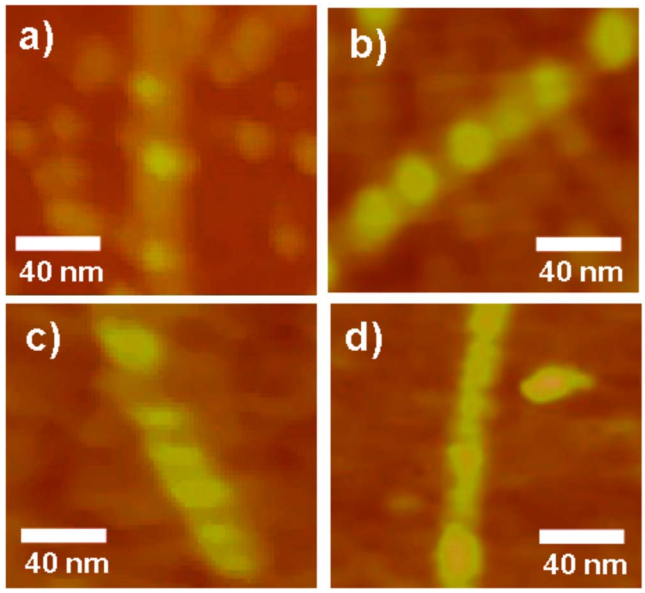

FIG. 3. (Color online) AFM image of four samples that were grown at different Si_2H_6 flow rate: (a) 1.1 SCCM, (b) 1.6 SCCM, (c) 1.8 SCCM, and (d) 2.1 SCCM.

QDs. This is due to the fact that with a higher flow rate there is more source material depositing over the substrate at any given time. More source impingement increases the opportunities for a Si atom to find a high strain point and settle to form a seed, which in turn will form a QD. This behavior has also been observed in QDs grown on HfO_2 patterned surfaces.[10] In contrast, if less Si is deposited then the chances for strain driven alignment are fewer and more QDs start to form over the rest of the substrate, as can be seen in Fig. 3(a). The size of each image is 200×200 nm^2. Due to tip deterioration some of the QDs appear larger in base than the others. Base size is dependent strictly on the size of the ridge created by the CNT since the formation of a valley at the edges of the CNT is expected to have a greater surface energy. This pattern of size limitation can be seen throughout the different flow rates in the QD growth. Figure 4(a) plots the linear density of QDs as a function of the gas flow rate.

Figure 4(b) shows the linear density of the QDs on CNT as a function of growth time. Coincidently the effects of time

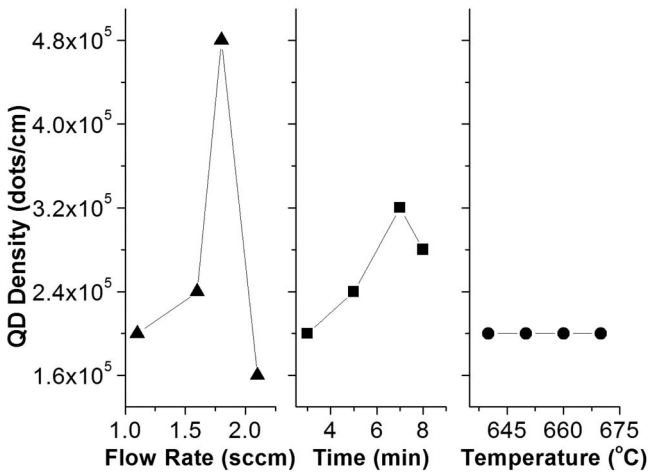

FIG. 4. Linear density of QDs on CNTs as a function of (a) flow rate, (b) growth time, and (c) growth temperature.

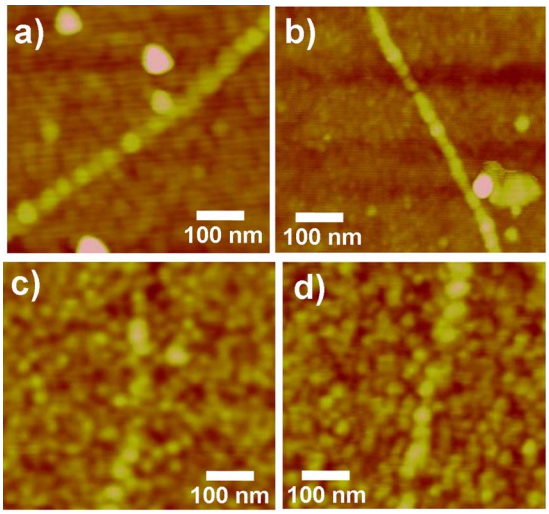

FIG. 5. (Color online) AFM images of four samples that have different hafnium oxide thickness: (a) 6 nm, (b) 7 nm, (c) 7.6 nm, and (d) 8 nm.

on the linear density resulted similar to the trend observed with varying the flow rate. The linear density increases with increasing time at the initial stage. For longer growth time, the QD density starts to decrease. The trend of the increase of linear density continues until the QDs exceed a certain size close to the width of the CNT ridge. The edge of the ridge is the threshold for the QD growth along the CNT. As the QD size reaches that threshold, the strain created by the CNT is compensated and growth past the edges of the 1D ridges is accelerated.

Figure 4(c) shows the growth temperature effect on the linear density of the dots on CNT. Interestingly different temperatures have a negligible effect on QD density in the window of alignment. Since growth temperature is known to affect adatom diffusion length,[15,16] it is reasonable for Si adatoms that are farther from CNT ridges in the initial stages of growth to migrate over to the alignment sites at higher growth temperature. In the examined temperature range, sufficient number of Si adatoms can migrate to preferential nucleation sites on 1D HfO_2 ridges on CNTs. Until the strain distribution along the 1D ridge becomes periodic, this is responsible for periodic aligned QDs. Such "cooperative" regimented growth mode was also observed when Ge dots were grown on 1D Si ridges.[8] This correlates with our low temperature results (not shown here) that show no alignment due to a low diffusion length. Another reason for a constant density with respect to temperature is that surface desorption of Si adatoms also increases with respect to temperature.[10]

To study different strain conditions created by the underlying CNT, we varied the oxide thickness. The effects created by the increase in oxide thickness can be seen in Figs. 5(a)–5(d). The thicker the oxide is, the sharper QDs are around the CNT ridge. This is due to the relaxation of the strain that forms along the top of the ridge structure. This in turn will decrease the selectivity of Si adatoms, forming more QDs on flat areas of the substrate. Although atomic layer deposition is conformal to most surfaces, CNTs are known to be nonreactive to the H_2O precursor.[13] Therefore many more HfO_2 layers are needed to be deposited to fully cover the CNT and have a smooth surface for good Si migration. The window of selectivity starts close to the 6 nm mark and decreases after 1– 2 nm depending on the size of the ridge, which is dependent on the diameter of the CNT.

In summary, we have successfully aligned Si QDs on strained HfO_2 covered CNTs. We studied the effects of growth temperature, disilane flow rate, and oxide thickness on the density of the QDs on the 1D HfO_2 ridges created by the underlying CNTs. We found that the size of the ridge created by the CNT dictates the maximum size of the QDs but the effect is diminished with the increase of the oxide thickness. In addition, the changes in disilane flow rate and growth time showed that the density of the QDs on the ridges can be controlled as well as the QD deposition outside of the ridges. These results show that the alignment of QDs by a bottom up approach to a size beyond CMOS ultimate limit is possible and controllable.

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