Void-mediated formation of Sn quantum dots in a Si matrix

Y. Lei,[a] P. Möck,[b] T. Topuria, and N. D. Browning
Department of Physics, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607-7059

R. Ragan,[c] K. S. Min,[d] and H. A. Atwater
Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California 91125

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Atomic scale analysis of Sn quantum dots (QDs) formed during the molecular beam-epitaxy (MBE) growth of Sn_xSi_{1-x} $(0.05 \leqslant x \leqslant 0.1)$ multilayers in a Si matrix revealed a void-mediated formation mechanism. Voids below the Si surface are induced by the lattice mismatch strain between Sn_xSi_{1-x} layers and Si, taking on their equilibrium tetrakaidecahedron shape. The diffusion of Sn atoms into these voids leads to an initial rapid coarsening of quantum dots during annealing. Since this formation process is not restricted to Sn, a method to grow QDs may be developed by controlling the formation of voids and the diffusion of materials into these voids during MBE growth. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1584073]

The interest in Sn quantum dots (QDs) embedded in a Si matrix is motivated by their potential applications as band structure engineered direct-band gap elemental semiconductors for optoelectronics and thermophotovoltaics.[1] As diamond structured α-Sn is a direct zero band gap semiconductor,[2,3] the formation of a substitutional Sn_xSi_{1-x} alloy is predicted to lead to a direct and tunable energy gap for $x>0.9$.[1] Quantum confinement is anticipated to increase and thus further tune the energy gap. The growth of ultrathin pseudomorphic Sn_xSi_{1-x} multilayers with $x=0.05$ and 0.1 by temperature-modulated molecular beam epitaxy (MBE) and *ex situ* annealing to form Sn-rich QDs has been reported previously.[4,5] However, the coarsening kinetics during post-growth annealing revealed an unexpected rapid increase of the average volume of the QDs in the first 2.2 h, though the subsequent growth slowed down to be linear with time.[5] Typically, any deviation from linear behavior is attributed to diffusion shortcuts related to defects (dislocations) in the material,[6] but in these samples the QDs nucleated in regions free from dislocations.[7] In this letter, we report an atomic scale study of α-Sn QDs in these materials[4,5] to elucidate the mechanism behind this initial rapid coarsening, which is of key importance to the overall properties of prospective devices. The implications for other QD systems will also be discussed.

The experiments were performed using a combination of *Z*-contrast imaging and electron energy-loss spectroscopy (EELS) in a 200 kV JEOL 2010F Schottky field emission scanning transmission electron microscope.[8] This microscope is capable of obtaining essentially incoherent *Z*-contrast images (intensity proportional to atomic number) in the scanning probe mode with a Scherzer resolution of ~0.13 nm. The EELS technique is exploited to quantify fluctuations in chemical composition, as changes in the intensity of core-loss signals give a direct measure of the quantity of specific elements.[9] Using the *Z*-contrast image as a map to position the probe for spectroscopy allows a direct correlation between the two techniques with atomic spatial resolution. The specimens for the microscopy study were prepared by standard thinning procedures.

Figure 1(a) shows a [110] cross-sectional *Z*-contrast image of the $Sn_{0.1}Si_{0.9}$/Si sample, indicating QDs with a diameter in the range of 7–10 nm were formed. Although the majority of the Sn-rich QDs are at the Sn_xSi_{1-x} layers, there are also QDs within the Si spacer layers, which typically appear to possess a tetrakaidecahedron shape bounded by {111} and {100} facets [Fig. 1(b)]. The formation of these QDs cannot be explained by the phase separation mechanism[5] that was proposed to operate within the Sn_xSi_{1-x} layers. Figure 2(a) shows another QD that has a particularly low intensity, i.e., low Sn content, instead of the essentially uniform brightness presented in Fig. 1(b). This QD also shows higher brightness at the edges, indicating that α-Sn lines its interface with the Si matrix. Since it is not

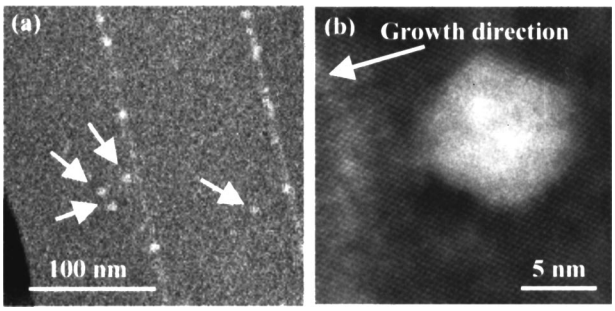

FIG. 1. [110] Cross-sectional *Z*-contrast images of: (a) the $Sn_{0.1}Si_{0.9}$/Si multilayer structure and (b) one QD within the Si spacer layers pointed by one of the arrows plotted in (a).

[a]Electronic mail: ylei1@uic.edu
[b]Present address: Department of Physics, Portland State University, P.O. Box 751, Portland, OR 97207.
[c]Present address: Hewlett-Packard Laboratories, 1501 Page Mill Rd., MS 1123, Palo Alto, CA 94304.
[d]Present address: Intel Corporation, California Technology and Manufacturing, MS RNB-2-35, 2200 Mission College Blvd., Santa Clara, CA 95052-8119.

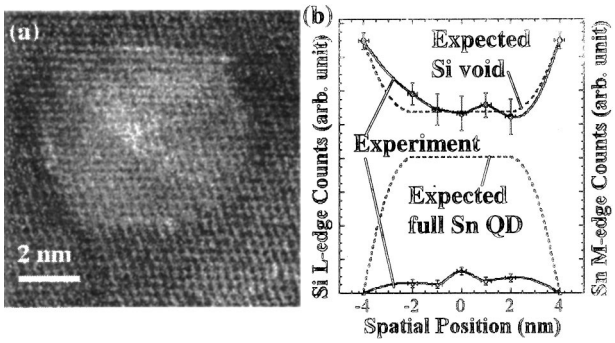

FIG. 2. (a) [110] Cross-sectional *Z*-contrast image of a QD within the Si spacer in the $Sn_{0.1}Si_{0.9}$/Si sample containing a very small amount of Sn. (b) Experimental results of Si *L*-edge counts (solid circles) and Sn *M*-edge counts (triangles) at the spatial positions along a line across the center of this QD and perpendicular to the growth direction, compared with two theoretical calculations when assuming this QD is an ideal void with no Si inside, and fully filled by Sn, respectively.

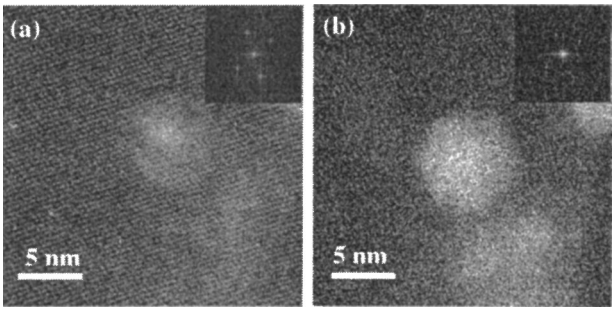

FIG. 3. [110] Cross-sectional *Z*-contrast images of a QD within the Si spacer layer in the $Sn_{0.05}Si_{0.95}$/Si sample (a) before and (b) after *in situ* heating at 300 °C for 3 h. Fast Fourier transform of the images at the corners indicate the Sn diamond structure remained same.

viable to determine the Si content inside the dot from the image intensity alone (as the size of the embedded QD is much smaller than the thickness of the matrix), in order to obtain the compositional information, a series of EELS spectra were acquired along a line across the center of this dot and perpendicular to the [001] growth direction. The Si *L*-edge intensity is plotted as solid circles in Fig. 2(b). The zero point on the spatial position axis corresponds to the position of the center, while the two edge points corresponds to the Si matrix around this QD. The plot indicates a sharp decrease of Si content within the QD relative to the Si matrix, as expected from a QD that contains Sn. However, further EELS analysis of the Sn content reveals that the drop in the Si concentration is much greater than the increase in the Sn content [the Sn *M*-edge intensity is plotted as triangles in Fig. 2(b)]. In this calculation, Sn atoms were assumed to occupy positions of Si atoms without lattice expansion, as no obvious lattice expansion was observed from the images. This implies that these QDs are voids in the Si matrix that are only partially filled. This is consistent with the equilibrium shape of a void in Si, which has been shown to be the same tetrakaidecahedron[10] shape shown in Figs. 1(b) and 2(a).

Two theoretical calculations on an ideal void and a QD fully filled by Sn were further performed and compared with the experimental results. Both this ideal void and QD were assumed to have the same size and shape as the original QD, and to be in a Si matrix of the same thickness in the experiment (this thickness has been calculated from the EELS spectrum).[11] After the shape parameters of this tetrakaidecahedron were determined based on the image, the effective thickness of Si along the [110] direction in the region containing this ideal void was calculated. The expected changes in the Si *L*-edge intensity are then plotted in Fig. 2(b), which shows the consistency with the experimental results. Similarly, the expected changes in Sn *M*-edge intensity in the case of a full Sn QD are also plotted [Fig. 2(b)], and the large discrepancy from the experiment verifies the assertion of a partially occupied Sn structure.

It has been observed that voids of ~10 nm in diameter and a number density of $\sim 10^{10}$ cm^{-2} can form ~10 nm below a fresh Si surface when it is exposed to air, due to the compressive strain induced by the growth of SiO_2 on the surface.[12] Thus, the appearance of voids in these multilayer materials is probably induced by the growth of Sn_xSi_{1-x} layers imposing a similar strain on the Si surface, and the thermal cycling during the growth[4,5] finally ensures preformed voids of any shape to grow and reach their equilibrium shape. Therefore, the initial rapid coarsening observed in Ref. 5 may be explained by diffusion shortcuts to these voids.

To confirm this hypothesis, a QD in the Si spacer layer of the $Sn_{0.05}Si_{0.95}$/Si sample was investigated during an *in situ* heating process performed at 300 °C for 3 h. The *Z*-contrast images taken before and after the heating indicate that the intensity within this QD increased (after being normalized according to Si matrix intensity) and became uniform, while it remained the same tetrakaidecahedron shape (Fig. 3). Although the lattice resolution was lowered a little due to the residual shaking of the heating stage, the fast Fourier transform of the image confirmed the Sn structure as diamond. Since this heating process is exactly analogous to the annealing used in the sample growth, the result is consistent with the QD initially being a void, to which the Sn diffuses during annealing. As the diffusion of Sn atoms into the voids in the Si matrix can further minimize the elastic strain energy between the Sn_xSi_{1-x} layers and Si matrix during the phase separation of the Sn_xSi_{1-x} layers, these voids are the preferential sinks for diffusing Sn atoms. Therefore, this void mediated mechanism dominates at the beginning of QD formation, and results in the initial rapid coarsening.

In conclusion, the analysis of Sn QDs in a Sn_xSi_{1-x}/Si multilayer system revealed a void mediated formation mechanism. The voids, created by the deposition of lattice mismatched Sn_xSi_{1-x} layers on the Si, are filled with endotaxially grown Sn to form pure α-Sn QDs. This mechanism explains the initial rapid increase of the size of QDs during postgrowth annealing, and is not restricted to Sn, as any material producing strain on the substrate may induce voids. It is noted that the results here are similar to previous studies that report the formation of hollow and partially filled precipitates in Si by ion implantation coupled with thermal treatments.[13–16] However, the size distribution of the precipitates is too wide to be suitable for device quality QD fabrication. By using MBE, the resultant voids have a well-defined shape and narrow size distribution. A method to grow uniform QDs may be developed by controlling the for-

mation of voids and the diffusion of materials into these voids during MBE growth.

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