Evolution of crystalline domain size and epitaxial orientation of CdTe/Si(111) quantum dots

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We have investigated the crystalline configuration of CdTe quantum dots (QDs) grown on hydrogen passivated Si(111) substrates by hot wall epitaxy. Coplanar and grazing incidence diffraction were used for determination of dot strain state and the vertical and lateral dimensions of the crystalline domain. A change in aspect ratio was observed as a function of dot size. X-ray diffraction (XRD) results show that despite a mismatch of almost 20% the islands grow with a fairly good epitaxial orientation with respect to the Si(111) substrate. The dot mosaicity was also determined and was found to decrease with island size from 7° to about 4° for the samples studied, indicating an improvement in epitaxial quality even before the island coalescence. Careful observation of CdTe(2 $\bar{2}$ 0) reflections in an azimuthal scan showed that an additional ensemble of islands is responsible for low-intensity peaks with a 30° symmetry besides the expected 60° symmetry. Transmission electron microscopy results have shown good accordance with atomic force microscopy and XRD and revealed the presence of an amorphous Tellurium rich oxide layer at the CdTe/Si interface, which could explain the fully unstrained QD state observed.

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I. INTRODUCTION

In recent years many semiconductor compound systems have been considered for quantum dot (QD) self-assembling due to their exciting electronic properties and potential applications in optoelectronic devices.^{1–4} However, most of this work has been concentrated in the III-V or IV systems, which follow the Stransky–Krastanov (SK) growth mode. Relatively little work has been performed on epitaxial II–VI QDs because of problems encountered in the growth process. However, the very large exciton binding energies makes the study of II–VI QDs particularly interesting due to their potential applications.^{5,6} The first studies on self-assembled CdTe islands date from 1996 and up to now almost all are concentrated in the ZnTe/CdTe system, which also follows the SK mode, although recent studies have shown that the II–VI compounds follow a modified SK mode, with a non-uniform or discontinuous wetting layer.^{7,8} Self-assembled QDs of II–VI compounds are also very attractive due to the possibility of magnetic ions incorporation and the promise for performing logic operations using electron spins.^{9,10} In this context the use of Si as substrate material has many advantages in comparison with GaAs, in spite the difficulties imposed by a very big lattice mismatch of 19.82%, and is an obvious goal due to its mechanical strength, low price and compatibility with standard Si-based device processing. Very recently, a study has demonstrated the growth of CdTe QDs

on Si(100) using ZnTe buffer layers¹¹ but there is a lack of reports on structural properties of CdTe grown directly on silicon.

In this work we focus on the structural study of uncapped CdTe self-assembled QDs grown directly on silicon(111) substrates. Previous work has shown, that in this case, the growth follows the Volmer–Weber (VW) growth mode, with three-dimensional (3D) islands nucleation since the early growth stages without the formation of a wetting-layer.¹² The obtained density and size dispersion are, nevertheless, comparable to those achieved by the SK mode, although following a peculiar temperature dependence, which seems to be a characteristic of the VW mode.^{13,14} However, there is still no information about the crystalline status of these QDs.

The samples studied were grown by hot wall epitaxy (HWE). Atomic force microscopy (AFM), transmission electron microscopy (TEM), coplanar, and grazing incidence x-ray diffraction (GID) were used in order to correlate island size, orientation, growth directions, shape, and strain. Despite the expected uncorrelated epitaxy, we have found that almost all CdTe nanocrystals follow the Si(111) orientation, with a residual amount of material exhibiting an in-plane lattice rotation of 30°.

II. EXPERIMENTAL

The HWE system consists of two independently controlled furnaces, used for source and substrate, and a shutter,

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placed within the 1 cm gap between the two furnaces, which controls the beginning and end of the growth process. The growth system was installed inside a Pyrex chamber and maintained at a pressure of about 5×10^{-7} Torr during the whole growth process. CdTe (5 N) was used as source material and maintained at 420 °C during the growth. At this temperature CdTe is known to evaporate congruently, with more than 98% of the vapor been composed by CdTe molecules.¹⁵ The resulting growth rate of 0.02 Å/s was determined by measuring the thickness of thick CdTe layers, using a stylus profiler. The Si(111) substrates were degreased, dipped in a 2% HF solution for 2 min and thoroughly rinsed in deionized water just before the introduction in the growth system, producing a passivated hydrogen-terminated Si surface. No substrate heat treatment was used before the growth. The procedure described above has been shown to produce 0.7 μm thick CdTe layers with rocking curve full width at half maximum (FWHM) of 288 arcsec, which indicate a good crystalline quality.¹⁶

For all samples investigated in this study, the substrate temperature was maintained at 300 °C since previous work has shown that this temperature results in higher QD densities and more uniform size dispersion,¹² from which improved crystalline island quality is also expected. We focus our attention in a series of four samples, grown with nominal thicknesses of 18, 72, 108, and 216 Å and labeled Sample A, B, C, and D, respectively.

The sample morphology was studied by *ex situ* AFM carried out on a MultiMode[®] AFM from Digital Instruments operating in TappingMode[®]. Phase Contrast images; suited to separate and identify closely arranged QD were also acquired simultaneously with the topographic images.¹⁷ Standard etched silicon tips with a nominal radius of curvature within the range of 5–10 nm were used to produce the images throughout this work.

The structural x-ray characterization was carried out at the Brazilian National Synchrotron Laboratory (LNLS) using coplanar diffraction and GID. Both Geometries are shown in Fig. 1. Switching between the two geometries is made by positioning the sample vertically or horizontally in a four-circle diffractometer. The x-ray photon energy was set to 10 keV. For GID measurements the incidence angle (α) was optimized by an independent circle for the maximum intensity of the CdTe peak, at the critical angle $\alpha_c = 0.24^\circ$. Using this geometry, we have measured both longitudinal ($\theta - 2\theta$) scans with radial momentum transfer given by $q_r = (4\pi/\lambda)\sin(2\theta/2)$ and transversal (θ) scans with angular momentum transfer given by $q_a = (4\pi/\lambda)\sin(2\theta/2)\sin(\delta)$, where δ is the difference in angle from the specular $\theta = 2\theta/2$ condition. With these scans one can address the in-plane lattice parameter $a_{||}$, dot lateral dimension (L) and island mosaicity (M). The $(2\bar{2}0)$ reflection, perpendicular to the (111) plane was chosen for all GID measurements, implying longitudinal momentum transfer positions of $q_r = 2,742 \text{ Å}^{-1}$ and $q_r = 3,272 \text{ Å}^{-1}$ (2θ angles of 31.397° and 37.676°) for bulk CdTe ($a = 6.482 \text{ Å}$) and Si ($a = 5.431 \text{ Å}$), respectively.

The in-plane island orientation was also investigated by performing long θ scans, spanning between 0° and 130° with

FIG. 1. Sketch of coplanar and GID geometries.

2θ fixed at the CdTe $(2\bar{2}0)$ position (39.526°). In order to determine the out of plane lattice parameter $a_{\perp}$ and the vertical island dimension (H) we have also used standard coplanar x-ray diffraction (XRD) measurements, addressing the CdTe(111) reflection. In all x-ray measurements the silicon peak, (111) or $(2\bar{2}0)$ was used as lattice parameter reference. All results reported are corroborated by measurements, not shown here, at the $(22\bar{4})$ reflections for GID and (333) reflections for standard coplanar diffraction.

TEM characterization was performed with a cross-section specimen oriented at $[211]$ silicon direction, prepared using manual and dimpler thinning, followed by Ar^+ ion beam precision polishing. A JEM-2100 LaB₆ TEM was used to obtain high resolution TEM images (HRTEM) and nano-beam electron diffraction (NBD) patterns (7 nm probe). A JEM-2100 FEG STEM with a GIF 863 Tridiem was used to obtain energy filtered TEM elemental images, filtering at 99 eV (Si-L_{2,3} peak), 404 eV (Cd-M_{4,5}), 532 eV (O-K), and 572 eV (Te-M_{4,5}) with the three window technique.

III. RESULTS AND DISCUSSION

As reported earlier, at the growth temperature used, CdTe deposits on Si(111) following the VW growth mode, with nucleation and growth of 3D islands without the formation of a wetting layer.¹² Figure 2 shows the AFM images for samples with increasing nominal thickness. In all images the total area is $3 \times 3 \mu\text{m}$ while the height full range is 10 nm for sample A and 70 nm for the other samples.

These pictures indicate a growth dynamics which initiate by the nucleation of 3D islands on the substrate surface. The surface area covered by CdTe islands, i.e., the surface coverage, follows a power law relation, which has been already reported for systems subjected to a diffusion-mediated nucleation and growth mechanism.¹⁸ Careful observation of Figs. 2(c) and 2(d), where the islands are large enough, shows that

FIG. 2. AFM images of samples with different growth times. Nominal thicknesses: (a) 18 Å, (b) 72 Å, (c) 108 Å, and (d) 216 Å. The scan size is $3 \times 3 \mu\text{m}^2$ and the height full scale is 10 nm for sample A and 70 nm for all others.

the islands have a triangular shape, a clear indication of a [111] axial orientation, as will be confirmed later.

AFM measurements performed in samples with higher coverage show that, as the growth proceeds, the QDs density and size get larger and after a given percolation limit islands start to coalesce until they completely cover the substrate, forming an epitaxial layer. Besides that, these measurements also show that the islands have a pyramidal shape with triangular base, as can be seen in Fig. 3. The formation of triangular pyramidal islands during the initial nucleation steps of CdTe/Si(111) films has already been observed by Lalev *et al.*¹⁹

In order to probe the crystalline quality and strain status of the islands, x-ray measurements were performed. Figure 4 shows a coplanar $\theta-2\theta$ longitudinal scan as a function of the longitudinal momentum transfer vector in the out-of-plane direction q_r performed on sample B. Using the Si(111) peak as the reciprocal lattice reference, we have determined an out of plane lattice parameter $a_{\perp} = 6.480(\pm 0.003)$ Å for CdTe islands. Similar results were obtained for all other samples

FIG. 3. (Color online) AFM image of a thick CdTe layer completely coalesced, showing a surface morphology with large triangular base pyramids. The height full scale is 200 nm.

FIG. 4. (a) Standard coplanar $\theta-2\theta$ diffraction pattern of (111) reflection for sample B. The solid lines are Gaussian fittings used to determine the FWHM.

indicating that the CdTe QDs are completely unstrained, independently of nominal coverage ($a_{\text{bulk}} = 6.482$ Å). The width of the CdTe peak in the longitudinal direction (Δq_r) has two different contributions: (i) strain broadening and (ii) crystalline domain size. This can be expressed as $\Delta q_r^2 = \Delta q_H^2 + \Delta q_S^2$, where Δq_H is the vertical size component and Δq_S is the strain component.²⁰ Since no strain has been measured for the CdTe islands we assume $\Delta q_S = 0$ and $\Delta q_r = \Delta q_H$. The FWHM of the CdTe(111) peak decreases as the coverage increases, reflecting the fact that the island size and therefore the coherent crystalline size increases with nominal coverage. The vertical island size can be estimated from these measurements using the relation $H = 2\pi/\Delta q_r$. We have observed an increase in vertical size H from 160 Å for sample A to about 500 Å for sample D. These values are in good qualitative agreement with the island height estimated from the AFM height ranges of Fig. 2. Therefore, x-ray measurements suggest that most of the islands are formed by a single crystalline domain with no defect inside or by very few crystalline domains.

Figure 5 shows results of the longitudinal ($\theta-2\theta$) and transversal (θ) grazing incidence diffraction measurements for sample C. Since the in-plane CdTe peak appears at the bulk value the FWHM of in-plane longitudinal scan (Δq_r) is

FIG. 5. Longitudinal and transversal scans for sample C.

TABLE I. Data obtained from the XRD measurements. A, B, C, and D are the sample labels, a_{ip} and a_{op} the in-plane and out-of-plane lattice parameter, respectively, H and L the vertical and lateral QDsize, respectively, and M the mosaicity.

	A (18 Å)	B (72 Å)	C (108 Å)	D (216 Å)
$a_{\perp}$ (Å)	6.474 ± 0.003	6.480 ± 0.003	6.484 ± 0.003	6.482 ± 0.003
H (Å)	160 ± 1	189 ± 2	378 ± 7	473 ± 11
$a_{\parallel}$ (Å)	...	6.476 ± 0.003	6.474 ± 0.003	6.475 ± 0.003
L (Å)	...	258 ± 3	264 ± 3	306 ± 4
M (°)	...	7.3 ± 0.2	4.8 ± 0.2	3.9 ± 0.2

directly used for determination of the lateral crystallite island size ($L = 2\pi / \Delta q_L$). In this case, similarly to the coplanar measurements, $\Delta q_r = \Delta q_L$, where Δq_L is the lateral size broadening component. The width $\Delta \theta_a$ of a transversal scan is the sum of a size component $\Delta \theta_l$ obtained from the longitudinal scan and a mosaic spread component M along the $(2\bar{2}0)$ direction. M can then be obtained using the relation: $\Delta \theta_r^2 = \Delta \theta_a^2 + M^2$.²⁰ For all samples studied the value of M is similar for $\{220\}$ reflection family.

Table I summarizes the data obtained from XRD measurements for all samples. Unfortunately, we were not able to measure the GID signal for sample A, due to the very small overall island volume and/or large island mosaic spread.

As discussed before, all determined lattice parameters indicate that the QDs are completely unstrained. Although both vertical and lateral sizes increase as the nominal coverage increases, it is possible to observe a change in QD aspect ratio with coverage. At low coverage, the lateral dimension is bigger than the vertical dimension but at higher coverage there is an inversion, with the lateral dimension becoming smaller than the vertical dimension.

This increase in QD aspect ratio observed for our samples is in agreement with a theoretical work about VW QDs by Müller and Kern²¹ and has already been observed for PbTe/BaF₂ QDs.²²

Finally, the existence of other island orientation was also probed by GID measurements. Figure 6 shows the result of a

FIG. 6. Long θ scan of sample B, showing that about 1% of the islands are rotated 30°. The inset shows the expected symmetry for the $\{220\}$ plane family.

FIG. 7. (a) HRTEM image of a CdTe/Si(111) island from sample B. (b) Island diffraction pattern from position No. 1 (inset). (c) Substrate nano-beam diffraction pattern from position No. 2 (inset).

long θ scan with 2θ fixed at the CdTe $(2\bar{2}0)$ position for sample B. The inset shows the expected symmetry of the $\{220\}$ plane family, showing that one should only observe diffraction peaks with 60° symmetry for perfect epitaxy. However, as can be clearly seen, there are also small intensity peaks with 30° symmetry, indicating that some islands are rotated by 30°. From the ratio of intensity between the peaks with 60° symmetry and the peaks with 30° symmetry it is possible to estimate the relative number of rotated islands. This number increases from about 1% to more than 3% from sample B to sample D, suggesting that nucleation of rotated islands may be enhanced by the defects generated during island coalescence, as the nominal thickness increases.

In order to probe the epitaxy of 30° rotated islands, TEM measurements were performed, showing a good accordance with AFM and GID results. Sample B characterization indicated an epitaxial oriented growth with a small fraction of islands rotated by 30°, as depicted on Fig. 7. Figure 7(a) shows a HRTEM image of a rotated island with 16 nm height. This image shows a clear evidence of an amorphous layer between the island and the substrate. The presence of this layer is surprising but could explain the unstrained state measured by GID experiments. Figures 7(b) and 7(c) present the NBD patterns. These NBD patterns were obtained at the positions indicated by No. 1 (island) and No. 2 (substrate) on Fig. 7(a), and can be indexed by $[110]$ and $[211]$ zone axis, respectively, and indicate the 30° rotation. Figure 8 shows the energy filtered TEM elemental mapping in a pair of superposed CdTe islands, obtained filtering at specific energies. These data are in agreement with the expected results for CdTe/Si(111) islands but also clearly indicate that the amorphous layer is predominantly formed by tellurium and oxygen. Oxygen can also be observed at island surface as a product of CdTe oxidation. The reason for the presence of this tellurium and oxygen rich amorphous layer at the QD/Si interface is not very clear. The silicon native oxide has been removed just before the growth and although the background

FIG. 8. Energy filtered TEM images at specific element low-loss energies: 99 eV (Si-L_{2,3} peak), 404 eV (Cd-M_{4,5}), 532 eV (O-K), and 572 eV (Te-M_{4,5})

pressure is just around 10^{-6} Torr, we don't believe that this oxide layer is formed during the growth. Inspection of other chemical map images (not shown here) shows the oxide layer not only between island and substrate but also along island's perimeter, indicating a postgrowth oxidation which occurs preferentially at tellurium rich regions, formed due to a Te-rich background pressure during the growth.

IV. CONCLUSION

In conclusion, we have used coplanar and grazing incidence XRD to investigate the evolution of crystalline structure of CdTe QDs grown directly on Si(111) as a function of growth time. Our results show that despite a mismatch of almost 20%, the produced QDs follow the substrate axial orientation. Using the silicon substrate XRD peaks as an internal reference, the measured island's lattice parameters (in-plane and out-of-plane) show that the dots are fully unstrained. Some islands show a rotation of 30° around the [111] axis, and the number of rotated islands increases as the nominal thickness increases. Transmission electron microscopy also corroborates these results.

It is surprising that, spite an almost 20% lattice parameter mismatch which should led to uncorrelated epitaxy, these CdTe islands exhibit the [111] orientation with sufficient crystalline quality to be detected by x-ray GID measurements. In fact, there has been numerous studies reporting successful growth of high quality thick epitaxial CdTe layers on Si but there is no consensus about which factors make it possible. Ebe and Takigawa have reported the observation of a 30° in-plane rotation slip for (111)CdTe epilayers grown on (111)Si substrates by metal-organic chemical vapor deposition depending on group VI to II ratio, which would reduce the mismatch to 3.4%.²³ There are also other studies on CdTe heteroepitaxy on Si using Si(100), Si(211), and highly misoriented Si(111) substrates which show some evidence of presence of a Te interfacial layer which would minimize the mismatch problem.^{19,24,25} Another study from Lalev *et al.*²⁶ shows the importance of the hydrogen passivated layer formed after the silicon dioxide removal in order to obtain high quality samples. Our data show evidence of both mechanisms: rotation and interfacial Te, although the Te layer observed occurs in an oxide state. However, they do not give direct insight about which one is the predominant

and, also, give no hint about the role of hydrogen. On the other hand, they do show that epitaxy with reasonable quality occurs since the very beginning of growth, pointing out to a post-growth oxidation of Te-rich regions below the islands, which would explain their final chemical status observed by TEM. We believe that our observations offer an important starting point for future studies in epitaxy of this system, using *in situ* techniques that could explore the behavior of the system in the low-coverage regime, such as low energy electron diffraction or scanning tunneling microscopy.

These results also show that it is possible to use the VW growth mode to obtain self-assembled CdTe/Si(111) epitaxial QDs with reduced mosaic spread and fairly good crystalline quality despite of a very large lattice parameter mismatch.

The understanding of the crystal quality evolution depicted here is crucial for further advance on the fabrication of CdTe self-assembled nanostructures on Si, as well as for shading light in the mechanisms that govern the VW growth mode.

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