Chapter I

Growth of the samples

We studied to type of quantum dots: self assembled QDs, which have remaining strain on it, and strain free QDs. The strained dots are formed by the relaxation of a CdTe layer on ZnTe. Strain free dots are formed by thickness variation of a CdTe quantum well between CdMgTe barriers.

I.1 Generality on Molecular Beam Expitaxy

The sample were grown using Molecular Beam Epitaxy (MBE). Cells of pure elements are heated to control their evaporation or until they reach sublimation. Those elements will formed the desired crystal on the substrate. They are kept in Knudsen cell, which consist of a crucibles of high-melting-point material with a low contaminating power (typically Pyrolytic Boron Nitride) wrapped in tungsten filament which will act as heater. Each are closed by a shutter controlled by a computer.

Upon reaching the right temperature, said shutter is opened to let the element travel to the substrate. The the camber containing the substrate is kept in Ultra High Vacuum (about 10^{-8} Pa), in order to avoid contamination of the sample and get a mean free path of the gas long compared to distance to the sample. This process is illustrated on Fig. I.1. Reaching the surface, the atoms diffuse before stopping, either having dissipated their kinetic through interaction with the surface, or (more commonly) being kept by island of previously deposited atoms. In the ideal case, the growth occur layer by layer, slowly (about 1 monolayer/s), giving a good control of the thickness of the grown material.

This necessity of Ultra High Vacuum kept the MBE to be developed before the end of the 1960s [1], although the the idea was formalized at the end of the 19th century. This method offers a good control on the growth, which make it useful for the development of nanostructure and nanoscience. The deposition layer by layer

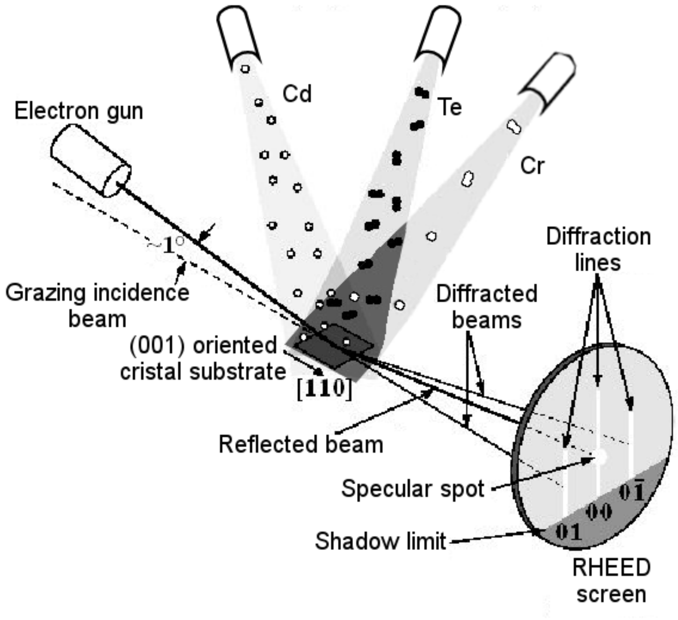

Figure I.1: Scheme of a MBE chamber and the position of the cells in regard of the substrate.

give the possibility to grow really thin structure, and the transition between two materials can be really abrupt, on a few monolayer (ML). Growing nano-structure is still the main use of MBE. However, this method is mainly on research purpose, its slow growth speed and hard to fulfil growth conditions being an obstacle for the industrialization of the process.

Another mode of MBE is used during the growth of the samples: Atomic Layer Epitaxy (ALE) or Migration-Enhanced Epitaxy (MEE). In this mode, only one element is opened at a time, growing the sample really layer by layer. Between each opening, the sample is left under vacuum in order to relax the surface. A full cycle correspond to opening each cell once. For CdTe, a substrate temperature between 260°C and 290°C guaranty a growth of only 0.5 ML for each cycle [2]. This allow a small uncertainty on the substrate temperature while keeping a really good control on the growth of the sample.

The growth was monitored with RHEED (Reflexion High-Energy Electron Diffraction). This technique requires a high vacuum, a given since MBE ask for ultra-high vacuum condition, and the use of an electron gun able to produce high energy electron. The beam of the gun is sent at low angle, between 1° and 3°, to the surface sample. This way, the electrons will only probe the surface of the sample, entering the material only on a 3 or 4 ML. Therefore the detected pattern directly gives information on the flatness and the crystallinity of the surface.

Incident electrons have a wave vector $\mathbf{k_i} = 2\pi/\lambda_e$, with λ_e the electron wavelength, typically 6 or 7 pm for an electron gun energy between 30 and 40 kV. Since only scattered diffraction is considered, the diffracted wave vector $\mathbf{k_f}$ as the same norm as the incident one $\mathbf{k_i}$. So the Ewald's Sphere has a radius equal to the norm of $\mathbf{k_i}$. In the reciprocal space, the plane of diffraction are infinite line. So, in the case of a perfect crystal, with a a perfect detector, the intersection with Ewald's sphere should be points. However, since the crystal can have some defect and neither the gun or the detector are perfect, the diffracted pattern present line, such as visible on Fig.I.3(b).

Once dots are grown, though, the surface become rough at the scale of the length of coherence of the beam. The electrons can interact with several more layer while passing through the dots. This can be seen on the diffraction pattern, where lines become points, such as shown on Fig.I.3(e).

Another use of the RHEED diffraction is the monitoring of the number of layer grown through ALE. Focusing on the lowest angle reflected spot, called the specular spot, one can see small variation in the reflected intensity during the growth, such as presented on Fig.I.2. This intensity is minimal when there is half a ML grown, and maximal when the ML is fully grown. This is due to the variation of reflectivity of the surface: maximal for a flat surface, minimal for a rough one. Therefore, a period of these oscillation is exactly the growth of a single monolayer [3, 4]. We can also see the relaxation of a layer, if the variation of intensity disappear at a point.

I.2 Strained dots: CdTe/ZnTE

I.2.1 Substrate preparation

The sample was grown on ZnTe(100) substrates. In order to get the bes surface to grow on, we need to clean the sample. Two cleaning methods were tested: etching of the sample in a Bromure solution, and exposition of the sample to a hydrogen radical plasma.

The etching process was done in four steps. All of them, except the etching in Bromure-ethanol, occur in an ultrasonic cleaning device vibrating the sample at 43kHz and last 3 minutes. We began with a cleaning in acetone, followed by one in ethanol. The third step was the actual etching: the substrate was put in a solution of Bromure-ethanol, with 3% of Bromure, during 1 minute. We finally rinsed it in methanol. Once rinsed, we keep the sample in ethanol until fixing them to the

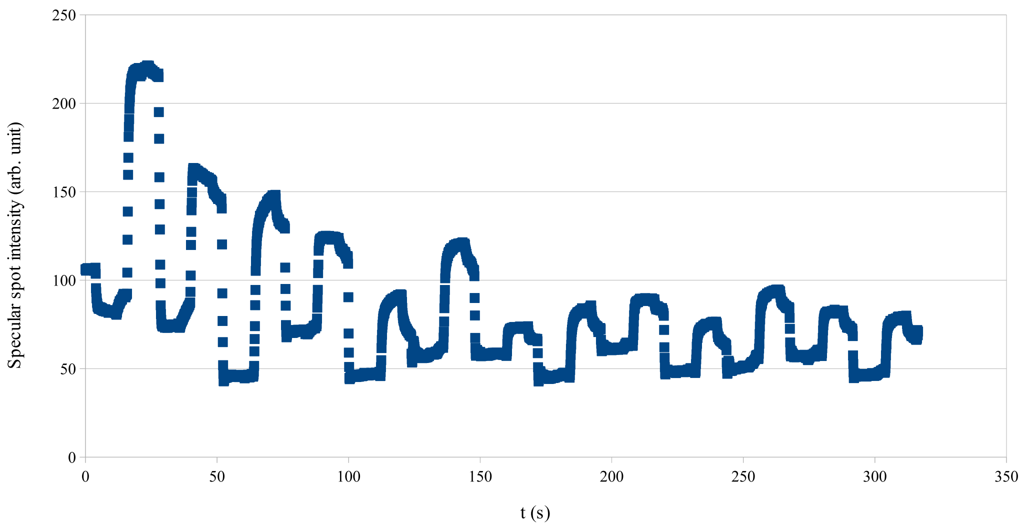

Figure I.2: RHEED oscillation for the ALE of strained dots.

sample holder. The growth usually occur the day after the cleaning, the sample being kept in the MBE load-lock chamber, under vacuum.

Another type of cleaning of the surface was tried: using hydrogen radical (H^*) to remove the impurity at the surface. This was done to get a smoother surface directly in the chamber, to avoid any contamination by the atmosphere that might occur during the transport from the etching room to the MBE chamber. In order to form the radical gas, a hydrogen gas was ionized in a chamber by a RF power source of 300 W and with a frequency of 13.6 MHz. This gas composition is optically checked by probing the emission of the Balmer series: for a pure hydrogen gas, peaks at 656 nm and 486 nm appear clearly. During the formation of this gas, the substrate temperature is raised to 400°C and we initiate its rotation. Once the plasma is formed, the valve to the main chamber is opened and the substrate is exposed to the plasma for 15 minutes. In order to check the quality of the surface, we look at the RHEED that should present strike.

I.2.2 Strained dots growth

The targeted flux chosen for the growth of the CdTe/ZnTe QD are presented in Tab. I.1 for each cell used during the growth of strained QDs. These flux were measured via the pressure gauge inside the MBE chamber. It was shown that the best quality of ZnTe was achieved for a growth in excess of Zn [5]. Otherwise, vacancies appear in the bulk, optically visible, and the surface is more rough.

Moreover, the adsorption power of the Zn is smaller than the Te. For these reason, we choose to grow the ZnTe barriers in excess of Zn.

Elements	Targeted BEP (Torr)
Cd	4.5×10^{-7}
Cr	N/A
Te	4.5×10^{-7}
Zn	6.8×10^{-7}

Table I.1: Aimed flux for each cell during the growth of the strained QDs.

The CdTe quantum dots was grown using ALE. When the sample is exposed to either Cd or Te, only one atomic layer will be deposited under each flux: we call this *auto-regulated* growth. The flux for both of the compound are therefore chosen to be the same [2].

Beginning the growth, the substrate temperature was initially raised to 320°C. The Zn cell shutter was open starting at 250°C, in order to flatten the surface for the growth. While it took several minutes to raise the substrate temperature, only one Zn layer was deposited due to the auto-regulation of the growth. When the substrate temperature reach 320°C, the Te shutter was also open, in order to grow the ZnTe buffer layer. This thick ZnTe layer guaranteed us to the best possible surface for the growth of the QD layer [6]. Once done, we set up the RHEED, growing a few more ZnTe level while searching the specular spot. The substrate temperature was then lowered to 170°C, the Zn cell being open until the temperature reach 250°C.

One of the main difficulty of this work was to calibrate the Cr flux in order to embed only a single Cr atom in most of the QDs of the sample. To achieve this, the Cr density must be of the same order as the QDs density at the surface of the sample. This means a really small flux, with a BEP of the magnitude of 10^{-10} Torr, which is about one order lower than the main chamber pressure and therefore not measurable with our technique. The optimisation was done starting with the know how acquired in Grenoble on the Mn and trying to optimise it for the Tsukuba machine, through a feedback loop with the micro-PL characterization in Grenoble.

This really small flux was achieved by heating the Cr cell around 1000K, low compared to its sublimation temperature, and opening the cell only once during the ALE, for only 5s. In order to have big enough QDs, emitting at right wavelengths, 6.5 ML of CdTe is the optimal CdTe thesis. However, the critical thickness of CdTe on ZnTe is 6.5 ML. Dislocations and defect will form in the layer for a higher thickness. Therefore, some sample were also grown with a 5.5 ML thickness

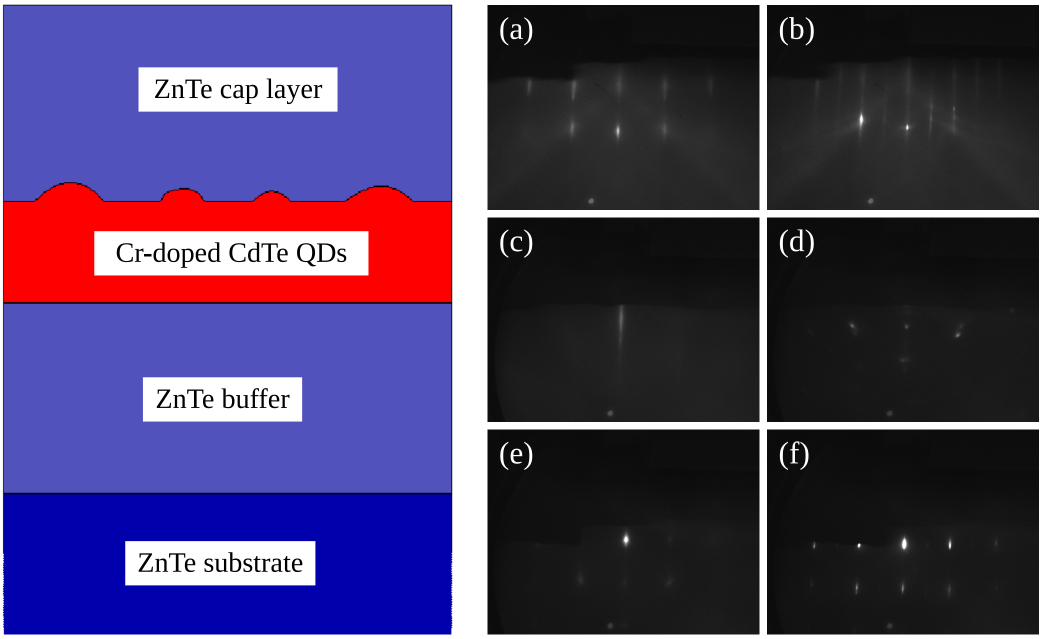

Figure I.3: Left: Layer structure of the strain Cr-doped CdTe QDs samples. Right: RHEED pattern taken at different key moment of the growth: (a) before the growth of the ZnTe buffer, (b) after the growth of the ZnTe buffer, (c) after the (Cd,Cr)Te ALE, (d) after the Te deposition, (e) during the Te evaporation (the picture was taken at $T_{substrate} = 177°C$) and (f) after the growth of the ZnTe cap.

in order to not get too close to the limit. At the chosen temperature, it correspond to either 13 cycles of ALE (for 6.5 ML) or 11 cycles (for 5.5 ML). The Cr cells was opened during the 7th cycle, halfway through the growth of the QD layer, in order to allow the Cr atoms to diffuse without going out the QD layers. The whole ALE recipe to grow the QDs layer is given in the Fig.I.4.

After the growth of the CdTe layer, we lowered the substrate temperature to 90°C to deposit the Te layer. It was deposited during 5 minutes. This step allows the CdTe layer to relax and form the quantum dots [7]. We then heated up the substrate again until 200°C, were we stayed for 20s in order to evaporate all the deposited Te [8]. If the dots were formed, we saw a spotty pattern like the one presented on Fig. I.3 (f). The Zn and Te cells were then opened, while the substrate temperature was raised to 240°C in order to grow a protective layer above the QDs.

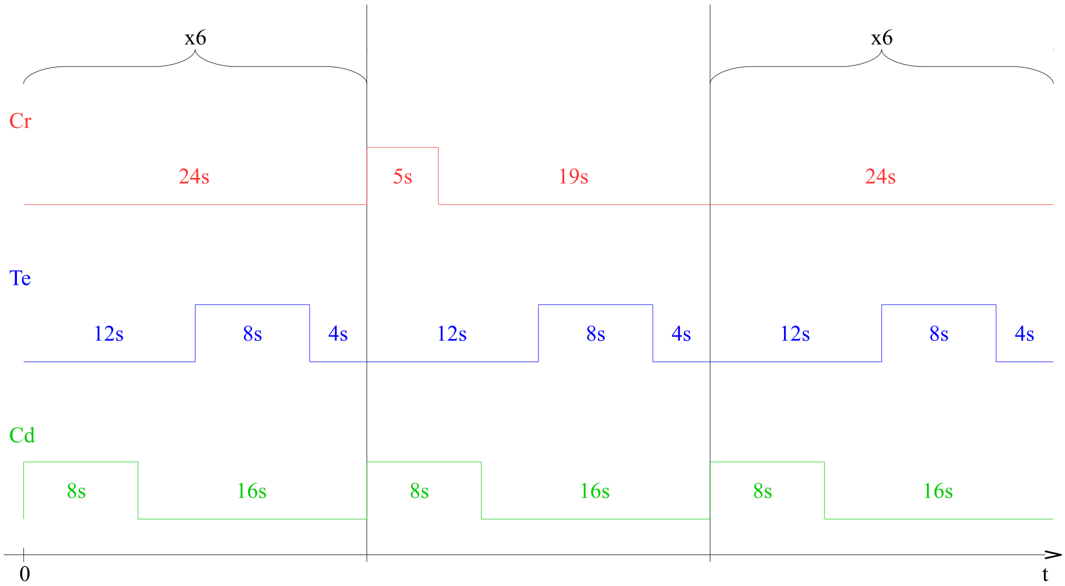

Figure I.4: Opening and closing cycles of each cell for the ALE of strained (Cd,Cr)Te samples.

I.2.3 Results

I.3 Other kind of samples

I.3.1 Charge control samples

Charge control samples are pretty straightforward. Instead of growing the sample on a non-doped ZnTe substrate, we do the growth on p-doped ZnTe substrate. Same steps are followed, but with thinner buffer and cap layers, in order to have a stronger electric on the dot layer. We chose to do both about 150 nm thick, calibrating with the ZnTe growth speed calculated via the RHEED oscillations.

Once the growth were finished, a thin, semi-transparent gold layer is deposited by sputtering. The samples are kept in nitrogen atmosphere during the transport. The exposition time of the sample in the sputtering machine was calibrated using gold deposited on GaAs substrate. Resistance of the gold layer was measured, and we chose the thinner thickness were we had a good conduction in the layer. Results are presented in Fig. I.5. We chose an exposition time of 35 s.

Table I.2: List of samples where Cr was found.

Sample	Type	Cleaning process	CdTe MLs	Cr aimed concentration (%)
dot358	Br etching	Strained dots	6.5	0.06
dot359	Br etching	Strained dots	6.5	0.11
dot363	Br etching	Strained dots	6.5	0.21
dot383	Br etching	Strained dots	5.5	0.19
dot385	Br etching	Strained dots	5.5	0.17
dot390	H^* plasma	Charge control	5.5	0.16

Figure I.5: Sample with Schottky gate and table of resistance versus gold thickness

Results

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The production of charged control samples was a success, and we could control the charge state of the dots found in. However, no Cr doped quantum were found. Some dots with Cr close to them were found. These are discussed in more in

Figure I.6: Example of charge variation

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I.3.2 Strain-free quantum dots

The barrier for strain free samples are made of CdTe. The chosen substrate for the growth was GaAs, on which we grew a layer of about 3 μm of CdTe. Growing such a thick layer guaranty that the remaining strain are in the order of 0.1% [9, 10]. Moreover, a small ZnTe layer was grown between GaAs and CdTe, which accelerated the relaxation of the strains [11].

For this sample, only a simple cleaning occur outside of the MBE machine. We did it in four steps, each of them lasting for 5 minutes in an ultrasonic cleaning device. We began with a cleaning acetone, at 43 kHz, followed by one in ethanol at the same frequency. We then put the substrate in water and clean it at 43 kHz. Finally, we changed the water and did the last step in water at 23 kHz, in order to clean the substrate from smaller dust particle.

Since the surface of the GaAs is oxidized, no RHEED pattern was visible, as shown on Fig I.7(a). The desoxidation was done in the MBE main chamber, in vacuum condition, using hydrogen radical (H^*). In order to form the radical gas, a hydrogen gas was ionized in a chamber by a RF power source of 300 W and with a frequency of 13.6 MHz. This gas composition is optically checked by probing the emission of the Balmer serie: for a pure hydrogen gas, peaks at 656 nm and 486 nm appear clearly. During the formation of this gas, the substrate temperature is raised to 400°C. Once the hydrogen chamber is full of H^* gas, we initiate the rotation of the sample. Since the chamber was situated just under the main and linked to her, we just had to open the shutter between the two to send the radical gas onto the substrate. We exposed the substrate to this gas for 15 minutes, under a pressure of about 6×10^{-7} Torr. We then checked the sample surface with RHEED, which should present a streak pattern with some dots as presented in Fig I.7(b).

Once the cleaning of the sample was finished, we closed the H^* gas chamber shutter, waited for the ultra-high vacuum to re-established in the main chamber and began the growth of the CdTe layer. We grew it in two times: one hour of growth just after the cleaning (described here) and about four hours just before the actual growth of the quantum dots structure.

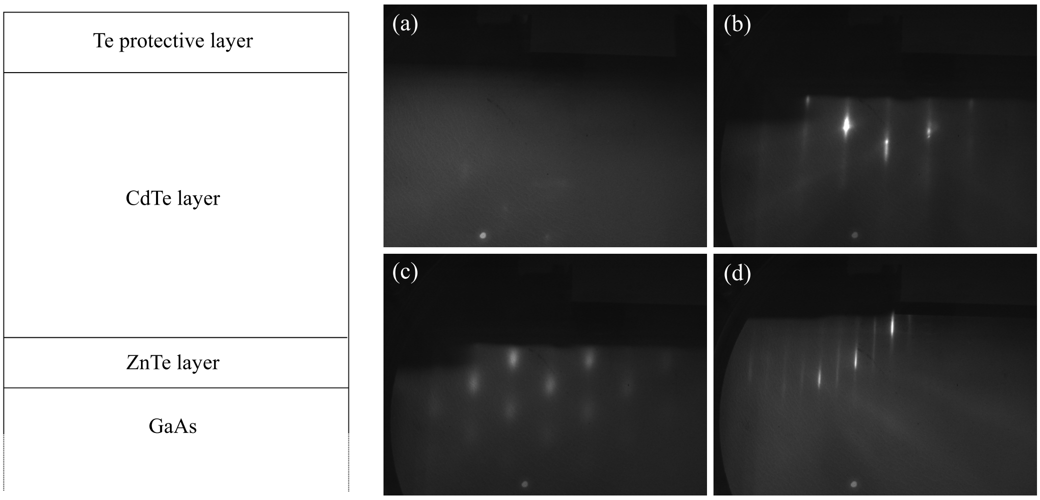

Figure I.7: Left: Layer structure of the hybrid substrate with its protective Te cap. Right: RHEED pattern taken at different key moment of the growth: (a) before H^* cleaning of GaAs, (b) after H^* cleaning of GaAs, (c) after the growth of the ZnTe layer, (d) after the growth of the CdTe layer.

This first part of the growth took place on a rotating sample. It only take about 15 ML of ZnTe on GaAs for the II-VI compound go back to its original lattice parameter [11]. Moreover, CdTe over ZnTe has a critical thickness of 5 ML [12]. So, to accelerate the relaxation of strain, we decided to grow a thing layer of ZnTe above the GaAs, before growing the CdTe thick layer. We lowered the substrate temperature to 320°C and opened the Zn cells for 30s with a BEP of 7.05×10^{-7} Torr in order to flatten the surface. We then opened the Te cells, with a BEP of 5.21×10^{-7} Torr, along with the Zn cell during 50s to grow the ZnTe layer in excess of Zn, making a layer about 7.2 nm thick.

We then went to the growth of the first CdTe layer. We lowered again the substrate temperature to 250°C, under Zn flux. Once stabilized at the temperature, we closed Zn cells and open the Cd and Te cells for 1h. The Te cell had the same flux as previously, while the Cd cells had a flux of 4.72×10^{-7} Torr. This layer was 633 nm thick, grown at 0.54 $ML.s^{-1}$. In order to protect the surface, we deposit an amorphous protective layer of Te above it, while decreasing the substrate temperature.

As said in the introduction, the strain free dots are formed by thickness variation of a CdTe QW surrounded by CdMgTe barrier. In order to have to good confinement while keeping a close enough lattice constant, we chose to use $Cd_{0.7}Mg_{0.3}Te$. Therefore, the first step of the growth was to chose the flux for the growth. We went through a process of trial and error, growing several samples and testing their composition with Electron Probe Mico-Analysis and X-Ray diffraction, as well as the thickness grown with a step gauge, in order to estimate the growth speed. Since we wanted to grow $Cd_{0.7}Mg_{0.3}Te$, we began the test with a ration Te:Cd of 1:0.7 and a ratio Te:Mg of 1:0.3. After five round of adjustment, we achieve the growth of $Cd_{0.7}Mg_{0.3}Te$, settling with the targeted flux presented in Tab.I.3. For the settled Mg flux, the step gauge indicated a grown thickness of 520 ± 5 nm. Since we grew the test layer during 1h, we found a growing speed of about 0.15 $nm.s^{-1}$.

Elements	Targeted BEP (Torr)
Cd	4.5×10^{-7}
Cr	N/A
Mg	1.6×10^{-8}
Te	5.26×10^{-7}

Table I.3: Aimed flux for each cell during the growth of the strained samples.

We began to heat the substrate temperature to 180°, in order to remove the protective amorphous Te layer. We waited a few second at this temperature to remove all the deposited Te, and then resumed the heating to go to 250°C. Starting at 200°C, we opened the Te cells in order to stabilize the surface. When the substrate temperature was stabilized at 250°C, we opened the Cd cells and grew a 2.35 μm layer of CdTe, in order to reach the thickness of the relaxation of strains for CdTe/GaAs [9, 10].

In order to be sure that there will be no relaxation in the quantum, we choose to stick to the maximum cumulated thickness of the CdTe on a CdZnTe lattice, which has been shown to be lower than the one of CdTe on a CdMgTe lattice. This correspond to a maximum cumulated thickness of 130 nm [13]. We chose to grow 40 nm below the QW, and 90 nm above it, in order to have a thicker protective layer.

Once the 40 nm barrier layer was grown, we lowered the substrate temperature under Te flux. Growing the QW layer in a Te environment smooth the surface layer of the sample and help having a flat surface to grow the well. Once the substrate temperature reach respectively 180°C (unmarked) or 195°C (marked), we began the ALE of the QW. [insert explication on the Cr SFD ALE here] The recipe is described in Fig.I.8. We then raised the substrate temperature up to

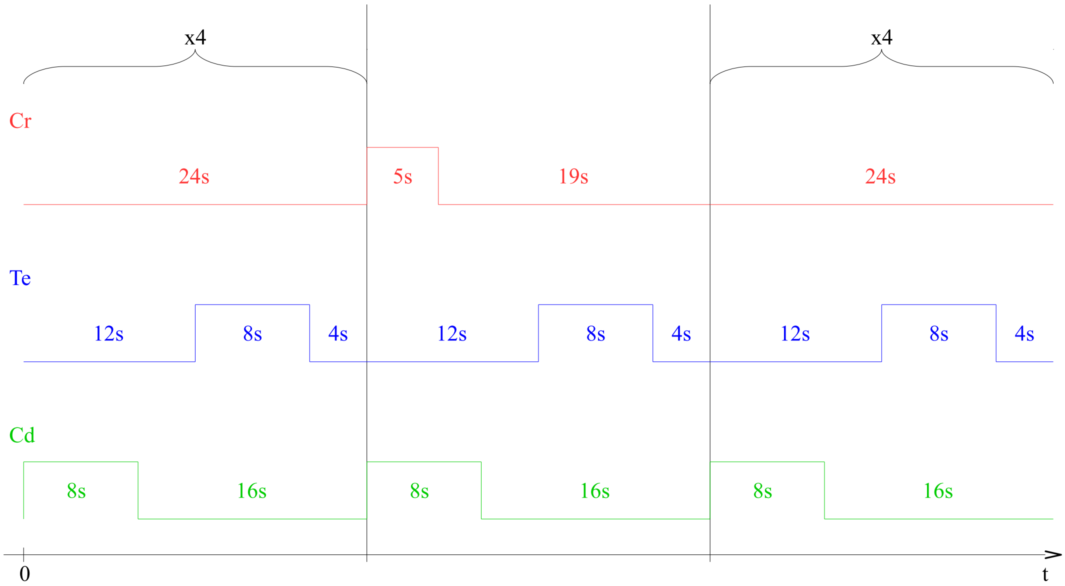

Figure I.8: Opening and closing cycles of each cell for the ALE of strain free (Cd,Cr)Te samples. (not accurate - 12/2015)

250°C, under a Te flux, in order to proceed to the growth of the upper barrier, acting also as a protective layer. The opening time was there calculated to grow 90 nm of $Cd_{0.7}Mg_{0.3}Te$.

Results

The sample presented thin and intense peaks. It hints at a better confinement of the carrier in the quantum than what have been expected from dots formed by the thickness variation of a quantum well. We tried to incorporate Cr in next samples, but no Cr-doped quantum dot were found in micro-spectroscopy. This is one kind of sample we should try to grow again in the future.

Table I.4: List of sample grown trying to incorporate Cr in SFD dots.

Sample	CdTe MLs	Cr aimed concentration (%)	Probability of Cr-doped QD
SFD4	4	0.35	None found
SFD5	2	0.15	None found
SFD6	2	0.54	None found
SFD7	2	0.35	None found
SFD8	2	0.75	None found

Figure I.9: Example of dot fin in SFD

Bibliography

[1] A. Cho and J. Arthur, "Molecular beam epitaxy", Progress in Solid State Chemistry **10**, 157–191 (1975).

[2] J. M. Hartmann, G. Feuillet, M. Charleux, and H. Mariette, "Atomic layer epitaxy of CdTe and MnTe", Journal of Applied Physics **79**, 3035–3041 (1996).

[3] J. Harris, B. A. Joyce, and P. Dobson, "Oscillations in the surface structure of Sn-doped GaAs during growth by MBE", Surface Science **103**, L90–L96 (1981).

[4] C. E. Wood, "RED intensity oscillations during MBE of GaAs", Surface Science **108**, L441–L443 (1981).

[5] R. D. Feldman, R. F. Austin, P. M. Bridenbaugh, A. M. Johnson, W. M. Simpson, B. A. Wilson, and C. E. Bonner, "Effects of Zn to Te ratio on the molecular-beam epitaxial growth of ZnTe on GaAs", Journal of Applied Physics **64**, 1191–1195 (1988).

[6] J. H. Chang, M. W. Cho, H. M. Wang, H. Wenisch, T. Hanada, T. Yao, K. Sato, and O. Oda, "Structural and optical properties of high-quality ZnTe homoepitaxial layers", Applied Physics Letters **77**, 1256–1258 (2000).

[7] F. Tinjod, B. Gilles, S. Moehl, K. Kheng, and H. Mariette, "II–VI quantum dot formation induced by surface energy change of a strained layer", Applied Physics Letters **82**, 4340–4342 (2003).

[8] P. Wojnar, C. Bougerol, E. Bellet-Amalric, L. Besombes, H. Mariette, and H. Boukari, "Towards vertical coupling of CdTe/ZnTe quantum dots formed by a high temperature tellurium induced process", Journal of Crystal Growth **335**, 28–30 (2011).

[9] K. Shigenaka, L. Sugiura, F. Nakata, and K. Hirahara, "Lattice relaxation in large mismatch systems of (111)CdTe/(100)GaAs and (133)CdTe/(211)GaAs layers", Journal of Crystal Growth **145**, 376–381 (1994).

[10] H. Tatsuoka, H. Kuwabara, Y. Nakanishi, and H. Fujiyasu, "Strain relaxation of CdTe(100) layers grown by hot-wall epitaxy on GaAs(100) substrates", Journal of Applied Physics **67**, 6860–6864 (1990).

[11] V. H. Etgens, M. Sauvage-Simkin, R. Pinchaux, J. Massies, N. Jedrecy, A. Waldhauer, S. Tatarenko, and P. H. Jouneau, “ZnTe/GaAs(001): growth mode and strain evolution during the early stages of molecular-beam-epitaxy heteroepitaxial growth”, Phys. Rev. B **47**, 10607–10612 (1993).

[12] J. Cibert, Y. Gobil, L. S. Dang, S. Tatarenko, G. Feuillet, P. H. Jouneau, and K. Saminadayar, “Critical thickness in epitaxial CdTe/ZnTe”, Applied Physics Letters **56**, 292–294 (1990).

[13] J. Cibert, R. André, C. Deshayes, G. Feuillet, P. Jouneau, L. S. Dang, R. Mallard, A. Nahmani, K. Saminadayar, and S. Tatarenko, “CdTe/ZnTe: critical thickness and coherent heterostructures”, Superlattices and Microstructures **9**, 271–274 (1991).