

Chapter I

Growth of the samples

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 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.

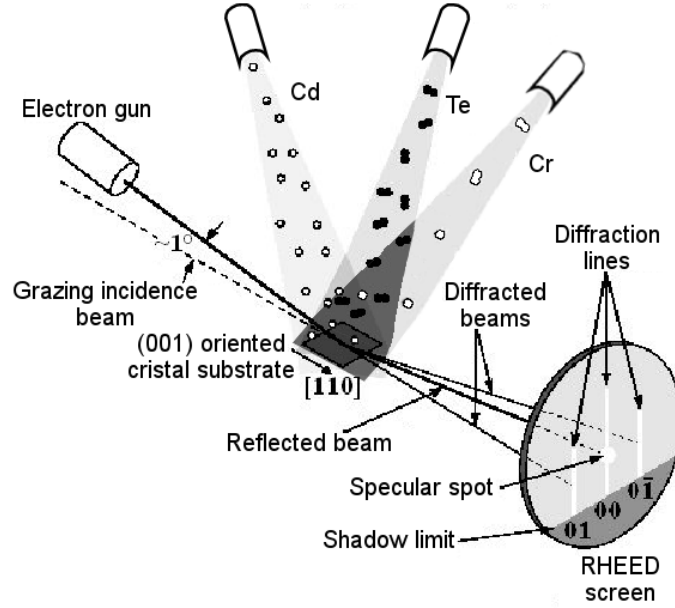


Figure I.1: Scheme of a MBE chamber and the position of the cells in regard of the substrate.

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. 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 require 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 electron 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 electron 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 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. Therefore, the reciprocal space of the crystal is not line anymore. 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, showing oscillation through, 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.

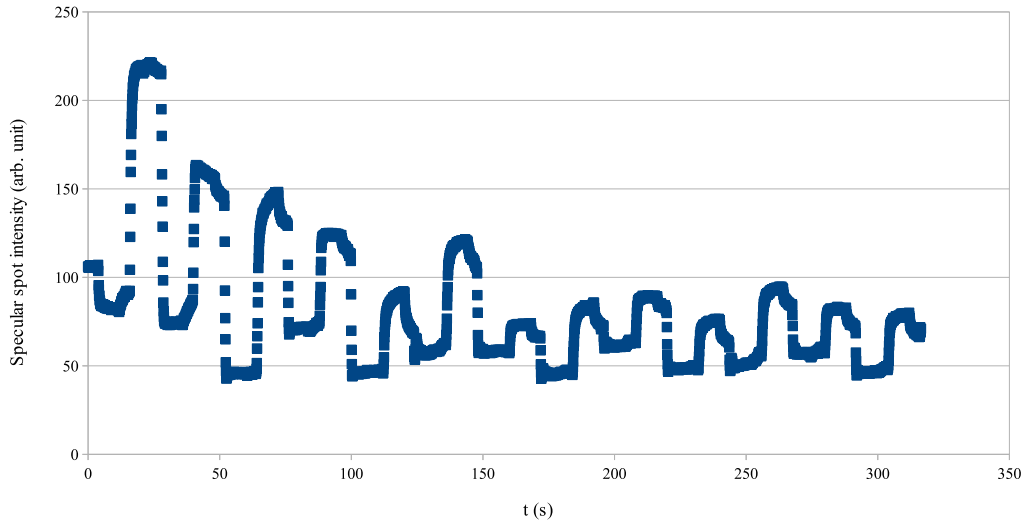


Figure I.2: RHEED oscillation for the ALE of strained dots.

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.2 Strained dots: CdTe/ZnTE

I.2.1 Substrate preparation

The sample was grown on ZnTe(100) substrates. We prepared the substrate by deoxidizing them through an etching process. It 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 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 sample holder. The growth usually occur the day after the cleaning.

I.2.2 Strained dots growth

Before beginning the actual growth, after we entered the sample in the main chamber, we had to heat the cells and the sample, and to do the flux calibration for each cell. The targeted flux and heating speed are presented in Tab.I.1 for each cell used during the growth of strained QDs.

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.

It was shown that the to have a good quality of material, it was better to grow the ZnTe 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.

When the sample is exposed to either Cd or Te flux during ALE, only one atomic layer will be deposited under each flux: we call this *auto-regulated* growth. So, we chose the same flux for both of the compound [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 can be deposited at a time. When the substrate temperature reach 320°C, the Te shutter was also open, in order to grow a ZnTe layer of about 420 nm, at about 0.4 ML.s⁻¹. 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 195°C (marked sample holder) or 180°C (unmarked sample holder), the Zn cell being open until the temperature reach 250°C. Then, the ALE began.

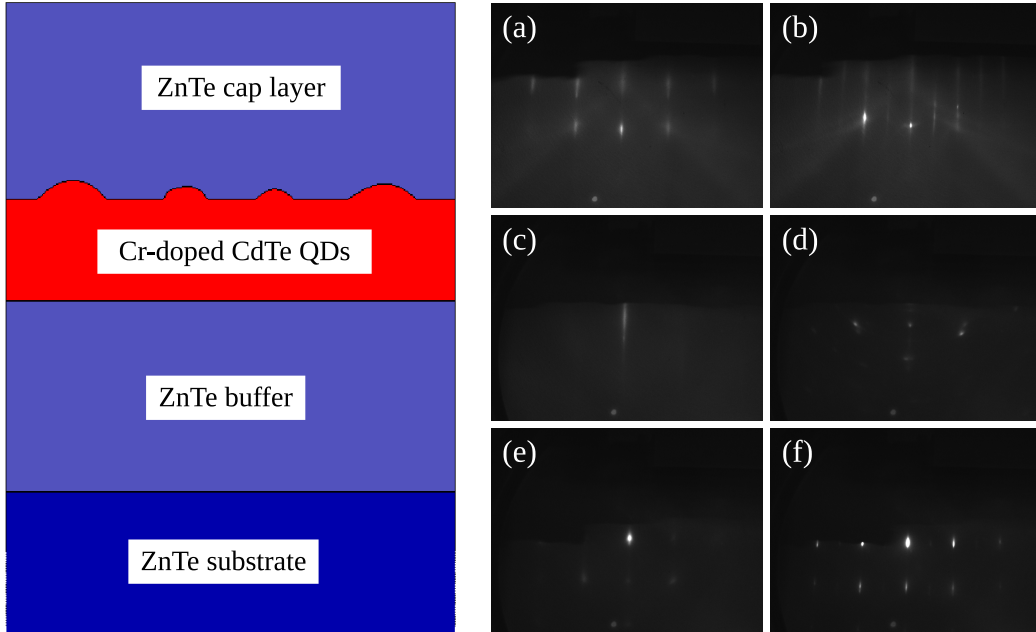


Figure I.3: Left: Layer structure of the strain Cr-doped CdTe QDs samples. Right: RHEED pattern taken at different key moment of the growth: (a) before the growth of the ZnTe buffer, (b) after the growth of the ZnTe buffer, (c) after the (Cd,Cr)Te ALE, (d) after the Te deposition, (e) during the Te evaporation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

One of the main difficulty of this work was to calibrate the Cr flux in order to trap only a single Cr atom in most of the QDs of the sample. To achieve so, 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 some 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 achieve 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, we needed 6.5 ML of CdTe. Going above this number will create dislocation and defects in the layer, preventing it to relax correctly to form the QDs. To do so, we had to do 13 cycles of Cd and Te cells opening, since each cycle grew half a layer. However, these 6.5 ML of CdTe don't relax naturally: we had to deposit Te above and evaporate before seeing the formation of the dots [7]. 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.

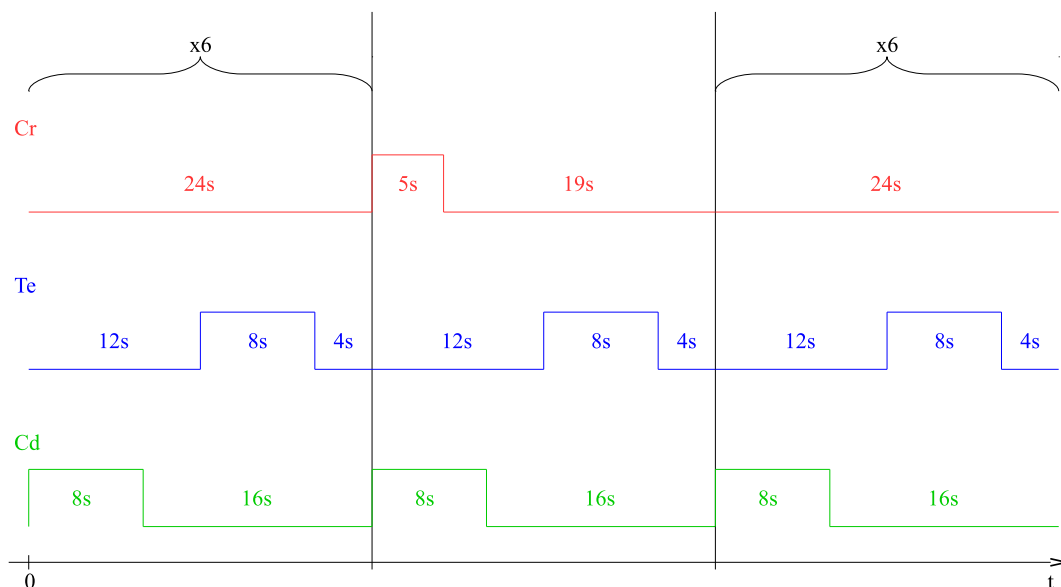


Figure I.4: Opening and closing cycles of each cell for the ALE of strained (Cd,Cr)Te samples.

Once the ALE was finished, we lowered the substrate temperature to 90°C to deposit the Te layer which formed the dots. It was deposited during 5 minutes. We then heated up the substrate again until 200°C, where 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 about 350 nm thick above the QDs.

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.



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

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.

Results

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Figure I.6: Example of charge variation

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 Sec. ??.

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 $3\text{ }\mu\text{m}$ 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.

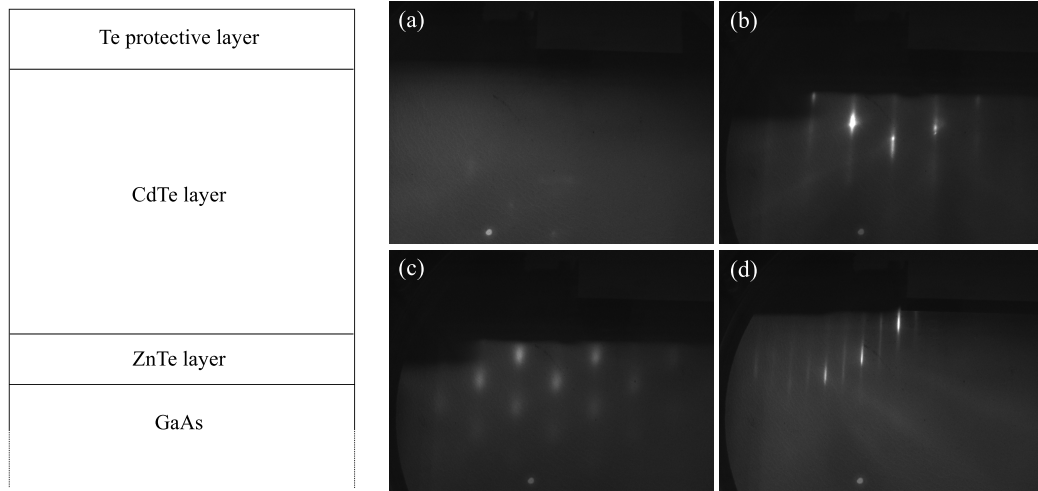


Figure I.7: Left: Layer structure of the hybrid substrate with its protective Te cap. Right: RHEED pattern taken at different key moment of the growth: (a) before H^* cleaning of GaAs, (b) after H^* cleaning of GaAs, (c) after the growth of the ZnTe layer, (d) after the growth of the CdTe layer.

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 thin 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 a good confinement while keeping a close enough lattice constant, we chose to use $\text{Cd}_{0.7}\text{Mg}_{0.3}\text{Te}$. Therefore, the first step of the growth was to choose the flux for the growth. We went through a process of trial and error, growing several samples and testing their composition with Electron Probe Micro-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 $\text{Cd}_{0.7}\text{Mg}_{0.3}\text{Te}$, we began the test with a ratio Te:Cd of 1:0.7 and a ratio Te:Mg of 1:0.3. After five rounds of adjustment, we achieved the growth of $\text{Cd}_{0.7}\text{Mg}_{0.3}\text{Te}$, settling with the targeted flux presented in Tab. I.2. 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.2: 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 seconds 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

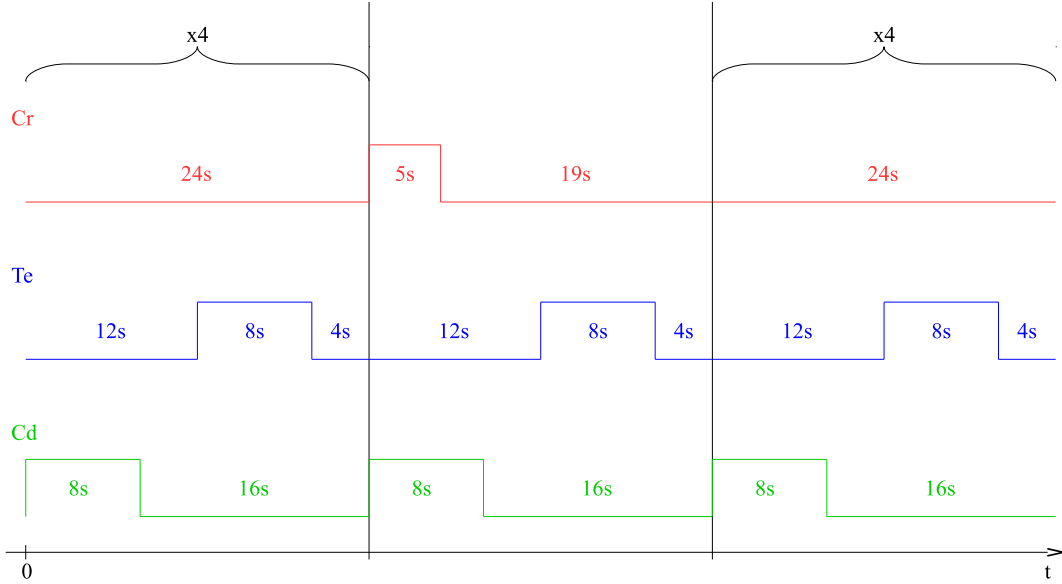


Figure I.8: Opening and closing cycles of each cell for the ALE of strain free (Cd,Cr)Te samples. (not accurate - 12/2015)

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 $\text{Cd}_{0.7}\text{Mg}_{0.3}\text{Te}$.



Figure I.9: Example of dot fin in SFD

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.

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