

Chapter VI. Conclusions and **Perspectives**

Selective growth of CdTe by molecular beam epitaxy on CdTe(211)B microseeds and Si(100) nanoseeds patterned on SiO₂ is demonstrated. The physisorption energy of CdTe on CdTe, Si and SiO₂ is considered as the driving mechanism to explain the selectivity during the growth.

VI.1. Summary of the results

VI.1.A. Substrate RCA cleaning and As passivation

A Si(111) substrate is cleaned ex-situ according to a well established RCA process. The result of the cleaning procedure is the formation of a thin oxide layer passivating the silicon surface. The sample is then loaded in a UHV environment in order to desorb the oxide by heating the substrate up to 1050°C. AES, LEED and STM experiments reveal that the resulting surface presents a 7x7 reconstruction and is free of contaminants.

The second step in the substrate preparation is to check the homogeneity of the As-passivation of the oxide-free silicon surface. The passivation ensures subsequent growth of CdTe with the B-polarity required to produce smooth surfaces of CdTe by MBE. Exposing the Si(111) substrate to As₄ flux before the oxide removal and during the cooling process from 1050°C up to 400°C leads to the formation of a (1x1)-As/Si(111) surface which is observed by STM and LEED. The LEED diffraction pattern is explained by considering a reciprocal space consisting of elongated dots (quasi 2D reciprocal space) instead of rods (associated to a perfect 2D reciprocal space).

These experiments confirm that the cleaning and passivation processes are well controlled and can be transposed to other substrates, such as Si(211).

VI.1.B. First CdTe selective growth study: CdTe(211)B seeds patterned on SiO₂

A 2 µm-thick CdTe(211)B/ZnTe(211)B/As/Si(211) layer is grown by MBE. Removal of the Si(211) native oxide and the As passivation are performed according to the procedure described in the previous section. ZnTe is grown with the substrate kept at 340°C by migration enhanced epitaxy. The CdTe layer is grown according to a two-step method: nucleation of a thin film at 340°C followed by growth of a thicker layer at higher temperature (440°C).

Optical lithography and wet etching are used to pattern this substrate. The resulting structure consists of CdTe pillars with a diameter ranging from 80 to 310 μm on a Si substrate. Because of air exposure, CdTe and Si are oxidized prior to loading in the UHV system. Selective growth is achieved by exposing the patterned substrate to a CdTe flux of $1.0 \cdot 10^{-7}$ mbar when the substrate is kept at 490°C: island's height and diameter are increased after CdTe exposure (measured by profilometry) while no CdTe is detected between the islands.

VI.1.C. Second CdTe selective growth study: Si(100) seeds patterned on SiO₂

SOI substrate is patterned by interferometric lithography to create Si(100) islands with an initial diameter of 300 nm on SiO₂. The patterned substrate is cleaned in a piranha solution and the resulting oxide is desorbed in UHV. A CdTe flux of $2.0 \cdot 10^{-8}$ mbar and a substrate temperature of 330°C are adequate conditions to achieve selective epitaxy: CdTe nucleates on Si(100) islands while nothing is adsorbed on the SiO₂ between the Si pillars. The selective growth is confirmed by AFM, SEM and XPS measurements.

VI.1.D. Selective growth mechanism

The selective growth process is explained by a difference in the physisorption energy of Cd or Te atoms impinging on CdTe, Si or SiO₂ substrate. The growth rate R can be written as a function of the flux F of atoms evaporated from a crucible of CdTe and adsorbed on the surface and the energies required to desorb from a physisorbed or a chemisorbed state (respectively E_{phys} and E_{chim}). Desorption is an Arrhenius process, so that:

$$R = F - a.e^{-\frac{E_{phys}}{kT}} - b.e^{-\frac{E_{chim}}{kT}} \quad (6.1)$$

In this equation, k is the Boltzmann constant and T is the substrate temperature. Experimental data to fit the growth rate can be obtained only for homoepitaxy of CdTe. For the growth of CdTe on Si and SiO₂, E_{phys} and b are adjusted so that a growth rate of 0 ML/s is obtained for a temperature of 480°C (under a flux of $1.0 \cdot 10^{-7}$ mbar of CdTe) and 310°C and 330°C (under a flux of $2.0 \cdot 10^{-8}$ mbar) on SiO₂ and Si respectively. The different values for F , a , b , E_{phys} and E_{chim} for the two studies on selective growth are presented in Table VI-1.

The parameter b represents the attempt frequency of chemisorbed atoms taking into account the fraction of adatoms in a chemisorbed state. The parameter a is also representative of the attempt frequency of the physisorbed atoms but because the proportion of atoms in the

physisorbed state is very low, the prefactor a is very small compared to b . This is due to the very short lifetime of an adatom in a physisorbed state.

	a (ML/s)	E_{phys} (eV)	b (ML/s)	E_{chim} (eV)
CdTe growth on CdTe	194	0.35	$2.7 \cdot 10^{12}$	1.90
CdTe growth on SiO₂	166	0.30	$2.7 \cdot 10^{12}$	1.90
CdTe growth on Si	166	0.31	$2.7 \cdot 10^{12}$	1.90

Table VI-1. Values of the parameters a , b , E_{phys} and E_{chim} for the growth of CdTe on CdTe, SiO₂ and Si.

It is also demonstrated that the temperature window to achieve selective growth depends on the impinging flux. Moreover, the width of the temperature window is larger for the CdTe on CdTe pillars system compared to the CdTe on Si seeds system.

VI.2. Perspectives

Selective epitaxy of CdTe on CdTe/Si and Si/SiO₂ systems was achieved. From the fundamental research aspect and technical point of views, several challenges should still be met:

- Numerous assumptions are made to elaborate the heteroepitaxy growth model of CdTe. Ab initio molecular dynamics studies could help in confirming the hypothesis on the physical events which are neglected in the desorption processes. Moreover, these calculations could be done to simulate the behavior of Cd and Te atoms on a SiO_x matrix, thus confirming the unchanged chemisorption energies of these adatoms on the surface compared to bare silicon;
- The cristallinity and the defect density on the CdTe pillars after the growth should be investigated and compared to these properties for usual 2D layers grown by conventional MBE. Because of the small size of the islands and the presence of non crystalline substrate between the islands, it is not possible to monitor the cristallinity by RHEED during the selective growth. For the cristallinity, a solution can be found in XRD with an incident beam from a synchrotron radiation beamline and focused on the sample (with a spot size diameter inferior to 1 μ m). For the distribution of the defects, dislocations are the most common defects and belong to the family of the extended defects. Hence they could be observed by PEEM if the Hg UV source is replaced by a He lamp or a synchrotron radiation producing photons of higher energy and by using an energy filter to discriminate the detected electrons. Hence cartography of the distribution of the workfunction can be established on the pillars and the defects could

be detected. If a thick layer is grown by selective growth so that the pillars coalesce, the strain partitioning between the substrate and the epilayer could be characterized by Raman spectroscopy and compared to the strain partitioning occurring in the conventional 2D growth;

- From the experimental results, it is obvious that the growth rate by MBE depends on the crystalline orientation. By choosing the adequate geometry of the initial pillar (both in size and in shape), one can expect the creation of nanostructures by MBE via the selective growth process. This can be used to study the properties of nanostructures and the conception of new design for third generation solar cells based on such nanoscale structures. For the initial size of the seed, it is demonstrated that the diameter has to be inferior to 100 nm to ensure a high efficiency of the relaxation mechanism induced by growing on structures accommodating in the three dimensions of space [12, 13]. Hence, electron beam lithography is probably the best candidate to pattern the initial seeds on the surface. Indeed, this revolutionary technique allows the patterning of structures in the nanometer range if the subsequent dry etching is well controlled. Additional fundamental research could be carried out to study the influence of the size and the orientation of the initial seeds on the resulting defect density, strain partitioning and cristallinity using the selective growth by MBE.