

Chapter II. Physical Properties of Si,
CdTe and ZnTe

II.1. Fundamentals of structural crystallography

II.1.A. Real space

A crystal consists of the infinite and periodic repetition, in the three dimensions of the real space, of a set of atoms around a point (node) of the lattice. A **unit cell** is a region of the crystal defined by three linearly independent vectors **a**, **b** and **c** which, when translated by any integral multiple of those vectors, reproduces a similar region of the crystal. Hence, it is possible to construct the whole crystal structure using a translation vector **T** so that:

$$\mathbf{T} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c} \quad (h, k, l \in \mathbb{Z}) \quad (2.1)$$

The **primitive unit cell** is the smallest cell (in volume) which is defined by the basis vectors **a**, **b** and **c**. However, in order to respect the symmetry of the crystal, it can be useful to define the basis vectors so that the unit cell is not the primitive one. According to the geometry of the crystal (related to the orientation and the length of the basis vectors), it is possible to define seven different unit cells called Bravais systems: triclinic, monoclinic, orthorhombic, tetragonal, cubic, hexagonal and rhombohedral (Figure II-1). Among each system, different positions and number of nodes can be found, leading to 4 different distributions in the unit cell: primitive unit cell P (one node at the end of each basis vector), body-centered unit cell I (one additional node at the center of the unit cell), base-centered unit cell C (one node at the center of two opposite faces of the unit cell) and face-centered unit cell F (one additional node at the center of each face). The possible combinations of the Bravais systems and the distribution of the nodes in the unit cell lead to 14 Bravais lattices according to the symmetry (Table II-1 and Figure II-1).

Symmetry of Bravais systems		
<i>Bravais systems</i>	<i>Bravais lattices</i>	<i>Symmetry group</i>
Triclinic	P	$\bar{1}$
Monoclinic	P, C	2/m
Orthorhombic	P, C, F, I	mmm
Rhombohedral	P	$\bar{3}m$
Tetragonal	P, I	4/mmm
Hexagonal	P	6/mmm
Cubic	P, I, F	m3m

Table II-1. Symmetry of Bravais systems [14].

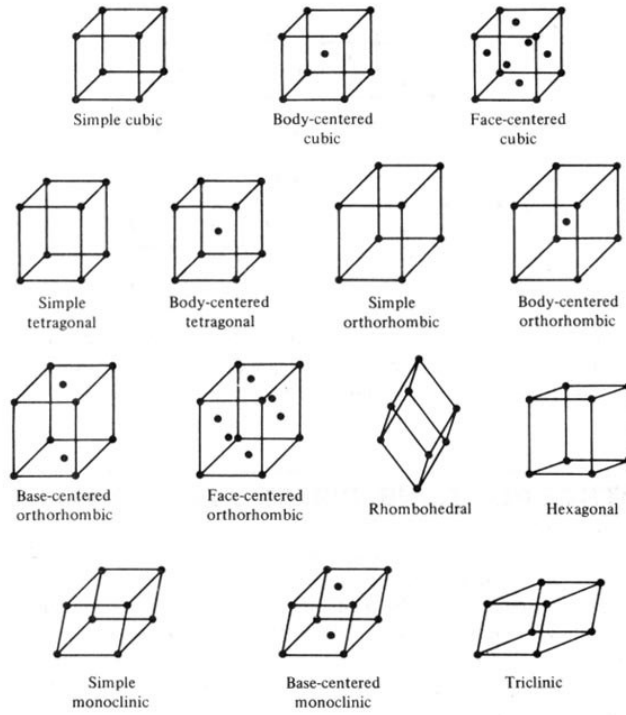


Figure II-1. The 14 Bravais lattices.

The semiconductors used in this thesis crystallize in the cubic structure, so all the theory hereafter is based on this specific crystallographic structure.

When the Bravais lattice of the crystal is determined via the choice of the 3 basis vectors **a**, **b** and **c**, it is possible to determine the position of each atom in the unit cell by a vector **r_j**:

$$\mathbf{r}_j = x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c} \text{ where } x_j, y_j, z_j \in [0,1] \quad (2.2)$$

For the cubic F type of Bravais lattices, two particular crystalline structures are defined: the zinc blende structure (for CdTe and ZnTe compounds) and the diamond structure (for Si). For the diamond structure, 2 atoms of Si are associated to each node of the cubic F lattice. These two atoms are in position (0,0,0) and (1/4,1/4,1/4) (Figure II-2a).

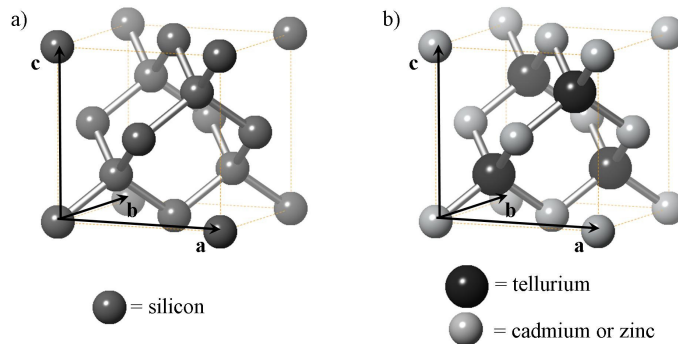


Figure II-2. a) Diamond structure of silicon; b) Zinc blende structure of CdTe and ZnTe.

For the zinc blende structure of CdTe and ZnTe, Cd (respectively Zn) atoms are at the (0,0,0) positions of each node of the cubic F structure and Te atoms are at the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ positions (Figure II-2b).

The general symmetry followed by ordinary cubic F crystals is modified for the diamond and the zinc blende structures. They belong respectively to the $Fd\bar{3}m$ and $F\bar{4}3m$ symmetry group.

II.1.B. Reciprocal lattice

Using the basis vectors in real space $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, one can define the basis vectors of reciprocal space $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$:

$$\begin{aligned}\mathbf{a}^* &= 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \\ \mathbf{b}^* &= 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \\ \mathbf{c}^* &= 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}\end{aligned}\tag{2.3}$$

The nodes of the reciprocal lattice are linked by a translation vector $\mathbf{G}$:

$$\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \text{ where } h, k, l \in \mathbb{Z} \tag{2.4}$$

The (hkl) indices are called Miller indices. In the real space, (hkl) represents the coordinates of the ending point of a vector whose origin is at a point (0,0,0) of the lattice. This representation is used to symbolize the atomic plane perpendicular to the (hkl) vector.

Reciprocal space is convenient for the analysis of diffraction patterns obtained by low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED) or X-ray diffraction (XRD). The intensity of the detected diffracted beams is explained by the structure factor [15] S_{hkl} :

$$S_{hkl} = \sum_{j=1}^n f_j \exp(-i\mathbf{G}_{hkl} \cdot \mathbf{r}_j) \tag{2.5}$$

In equation (2.5), n is the number of atoms in a unit cell, $\mathbf{G}_{hkl}$ is the vector of the reciprocal lattice (see equation (2.4)), $\mathbf{r}_j$ (defined by equation (2.2)) and f_j are respectively the position and the atomic form factor of the j^{th} atom in the unit cell. The atomic form factor describes the influence of the electronic density of the atom in the surrounding space. This factor is related to the nature of the atom and represents the diffracting power of the j^{th} atom. The detailed expression of the form factor also depends on the nature of the particles constituting the beam

diffracted by the crystal (beam of X-rays, electrons, ions or neutrons). The form factor and the diffracted intensity are discussed in Chapter V for X-rays and electrons.

For a primitive unit cell composed of 2 identical atoms and according to the structure factor (equation (2.5)), diffraction can be observed if the argument of the exponential term is equal to 1, i or -i. Hereafter, the diffraction conditions are explained for two crystallographic structures composed of two atoms per unit cell: the diamond structure of silicon and the zinc blende structure of CdTe and ZnTe.

II.2. Study of silicon crystal

II.2.A. Electronic and optical properties

Silicon is and has been a widely used substrate for the growth of CdTe and MCT. It is then interesting to study its crystallographic properties. In this section, the most common faces for subsequent growth of CdTe or MCT are studied: Si(100), Si(111) and Si(211).

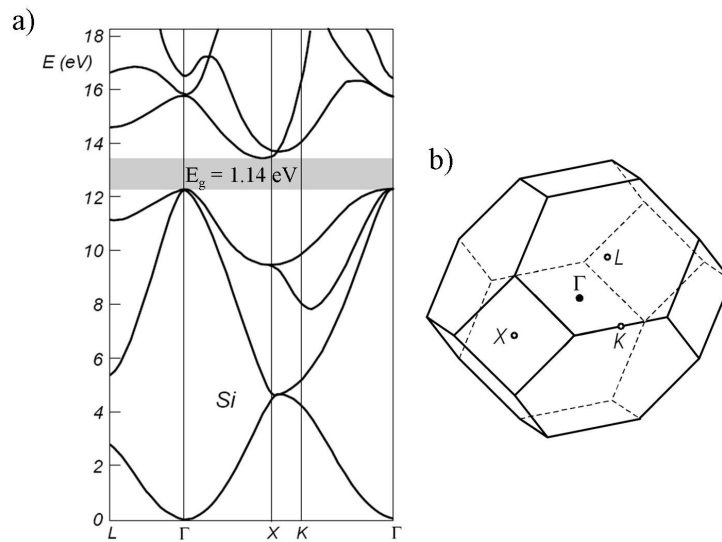


Figure II-3. a) Band structure; b) Brillouin zone of silicon [16].

Silicon crystallizes in the diamond structure with a lattice parameter of $5.43 \text{ \AA}$ at room temperature. This semiconductor has an indirect bandgap of 1.14 eV at room temperature which is in the very-near IR region (Figure II-3). Compared to direct bandgap semiconductors, the probability of absorption in an indirect bandgap semiconductor is lower. Indeed, the absorption of a photon has to be correlated to the absorption or the emission of a phonon to fit the difference in momentum between the electron emission state level in the conduction band and the electron collection state level in the valence band. This is due to the

fact that the momentum of a photon is much smaller than that of a phonon because of the difference in the particle mass (even if speed of a photon is the light speed compared to the sound speed for a phonon). Hence, the absorption process in an indirect bandgap semiconductor involves three particles (electron – photon – phonon) whereas only two particles interact together in a direct bandgap semiconductor (electron – photon). As a result, the absorption probability is higher for direct bandgap semiconductors and indirect bandgap semiconductors are poor photon absorbers. Because of that, if Si is used as a substrate for CdTe and if the final device is back illuminated, the adsorption of the Si substrate is negligible.

II.2.B. Crystallographic structure in the real space

II.2.B.1 Si(100)

Si(100) face presents a 4-fold symmetry (Figure II-4a). Each atom is bound to 2 atoms of the upper layer and 2 atoms of the lower layer. These two bonds are rotated by 90° to each other (Figure II-4c). Since the atoms at the Si(100) surface have 2 dangling bonds (Figure II-4b), the surface is highly reactive to the particles in the surrounding environment. A (2x2) or a c(4x4) reconstruction of the surface decreases the number of dangling bonds.

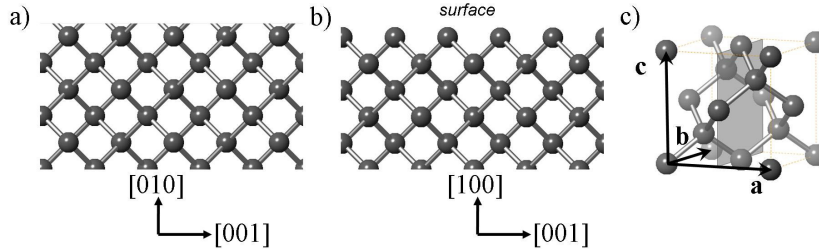


Figure II-4. Unreconstructed Si(100) in a) [100] direction and b) [010] direction; c) Si(100) plane.

II.2.B.2 Si(111)

The Si(111) face has a 6-fold symmetry (Figure II-5a) and each atom of the surface presents one dangling bond (Figure II-5b) leading to a highly reactive surface. The Figure II-5c presents an atomic plane of Si(111). If the Si(111) surface is annealed at high temperature (above 900°C), the surface shows a (7x7) reconstruction to decrease the number of dangling bonds.

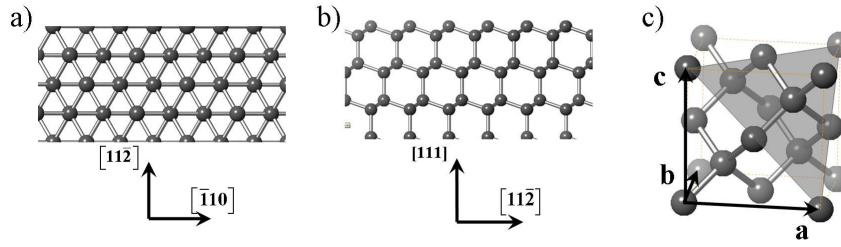


Figure II-5. a) Top view of Si(111); b) side view of Si(111) in the $[110]$ direction; c) Si(111) atomic plane.

II.2.B.3 Si(211)

Unlike the two previous orientations, the Si(211) surface has no symmetry axis. The (211) orientation is composed of Si(111) and Si(100) terraces tilted respectively by an angle of 19.47° and 35.26° from the (211) plane (Figure II-6a and b). The periodicity in the $[\bar{1}11]$ direction is $9.41 \text{ \AA}$. The atoms at the surface contain dangling bonds, making this surface highly reactive without passivation process. Figure II-6c presents the (211) atomic planes of this orientation. A (2×1) reconstruction of the surface decreases the dangling bond density.

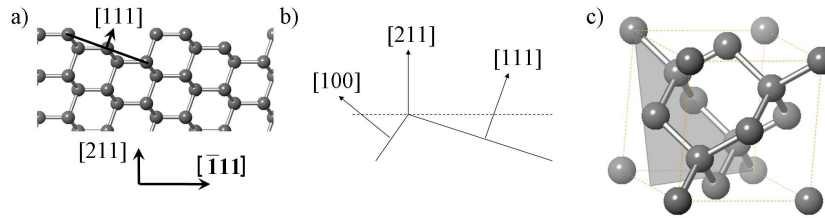


Figure II-6. a) Si(211) observed in the $[110]$ direction; b) Schematic representation of the stepped Si(211) surface; c) Si(211) atomic plane.

II.2.C. Crystallographic structure in the reciprocal space

The diamond structure is a particular case of the ideal face-centered cubic structure with two atoms taken into account instead of one: one atom in position $(0,0,0)$ and another one in position $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

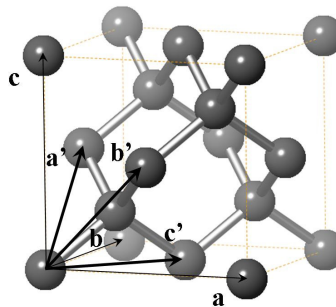


Figure II-7. Basis vectors of face-centered cubic structure (a, b, c) and of the primitive cell (a', b', c').

For the standard face-centered cubic structure and using the structure factor in order to determine the condition on (hkl) so that the sum of the exponential terms is zero in (2.5) (i.e. systematic extinction), totally destructive interference is observed if the Miller indices do not have equal parity. In the case of the diamond structure, an additional condition for systematic extinctions has to be determined. From the three basis vectors of the face-centered cubic structure **a**, **b** and **c**, it is possible to build the three vectors of the primitive unit cell **a'**, **b'** and **c'** such that (Figure II-7):

$$\begin{aligned} \mathbf{a}' &= \frac{\mathbf{b} + \mathbf{c}}{2} \\ \mathbf{b}' &= \frac{\mathbf{a} + \mathbf{c}}{2} \\ \mathbf{c}' &= \frac{\mathbf{a} + \mathbf{b}}{2} \end{aligned} \quad (2.6)$$

Using (2.3) and (2.6) the basis vectors **a****, **b**** and **c**** of the primitive cell in reciprocal space can be expressed as a function of the reciprocal vectors **a***, **b*** and **c*** (with a length of $2\pi/a_0$) constructed from vectors **a**, **b** and **c**:

$$\begin{aligned} \mathbf{a}^{*'} &= -\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^* \\ \mathbf{b}^{*'} &= \mathbf{a}^* - \mathbf{b}^* + \mathbf{c}^* \\ \mathbf{c}^{*'} &= \mathbf{a}^* + \mathbf{b}^* - \mathbf{c}^* \end{aligned} \quad (2.7)$$

These vectors demonstrate that the reciprocal lattice is a body-centered cubic structure (I-type). To give an analytical expression for the structure factor, we consider the reciprocal lattice points as $\mathbf{G} = h'\mathbf{a}^{*'} + k'\mathbf{b}^{*'} + l'\mathbf{c}'$ and the position of the 2 atoms in the (**a'b'c'**) system in positions (0,0,0) and (1/4,1/4,1/4) as $\mathbf{r}_j = u_j'\mathbf{a}' + v_j'\mathbf{b}' + w_j'\mathbf{c}'$. In the equation (2.5), f_j is the same for each atom of the diamond structure. Then, the structure factor of silicon can be written as:

$$S_{hkl} = f_{Si} \left[1 + e^{-i2\pi \left(\frac{h'+k'+l'}{4} \right)} \right] \quad (2.8)$$

Hence, the existing conditions of the structure factor can be easily calculated:

$$S_{hkl} = \begin{cases} 2f_{Si} & \text{if } h' + k' + l' = 4n \\ f_{Si} - if_{Si} & \text{if } h' + k' + l' = 4n + 1 \\ f_{Si} + if_{Si} & \text{if } h' + k' + l' = 4n + 3 \\ 0 & \text{if } h' + k' + l' = 2(2n + 1) \end{cases} \quad (2.9)$$

It is more usual to use the (**abc**) and (**a*b*c***) basis vectors for the real and reciprocal lattices respectively. Using equations (2.6) and (2.7), and writing $\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ and $\mathbf{r}_j = u_j\mathbf{a} + v_j\mathbf{b} + w_j\mathbf{c}$, we can conclude that:

$$\begin{aligned}
1) \mathbf{G} &= h'\mathbf{a}^* + k'\mathbf{b}^* + l'\mathbf{c}^* \\
&= h'(-\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*) + k'(\mathbf{a}^* - \mathbf{b}^* + \mathbf{c}^*) + l'(\mathbf{a}^* + \mathbf{b}^* - \mathbf{c}^*) \\
&= (-h' + k' + l')\mathbf{a}^* + (h' - k' + l')\mathbf{b}^* + (h' + k' - l')\mathbf{c}^* \\
2) \mathbf{G} &= h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*
\end{aligned}$$

Comparing 1) and 2), we obtain that:

$$\left. \begin{aligned} h &= -h' + k' + l' \\ k &= h' - k' + l' \\ l &= h' + k' - l' \end{aligned} \right\} \text{or } h + k + l = h' + k' + l'$$

So the structure factor can be written as:

$$S_{hkl} = \begin{cases} 2f_{Si} & \text{if } h + k + l = 4n \\ f_{Si} - if_{Si} & \text{if } h + k + l = 4n + 1 \\ f_{Si} + if_{Si} & \text{if } h + k + l = 4n + 3 \\ 0 & \text{if } h + k + l = 2(2n + 1) \end{cases} \quad (2.10)$$

In conclusion, two conditions can lead to a systematic extinction:

- If the Miller indices don't have the same parity (derived from the ideal face-centered cubic structure);
- If the sum of the Miller indices is the double of an odd number (derived from the particular case of the diamond structure).

II.3. Study of CdTe and ZnTe crystals

II.3.A. Electronic and optical properties

CdTe and ZnTe have a lattice parameter of respectively 0.648 and 0.610 nm and a direct band gap of 1.56 eV for CdTe and 2.25 eV for ZnTe (Figure II-8a). The associated band structures in the direction of high symmetry of the zinc blende crystal (Figure II-3b) are presented in Figure II-8b and c. Because of the direct bandgap, the weak momentum associated to the photon is not a limitation for the electronic transition to promote an electron from the top of the valence band to the bottom (or higher) of the conduction band. Note that from figure a), CdTe is a good substrate for MCT growth because the lattice parameter of HgCdTe varies between the lattice parameter of CdTe and HgTe. From the Hg/Cd ratio, the band gap of MCT can be tuned from 0 to 1.56 eV (in the IR range).

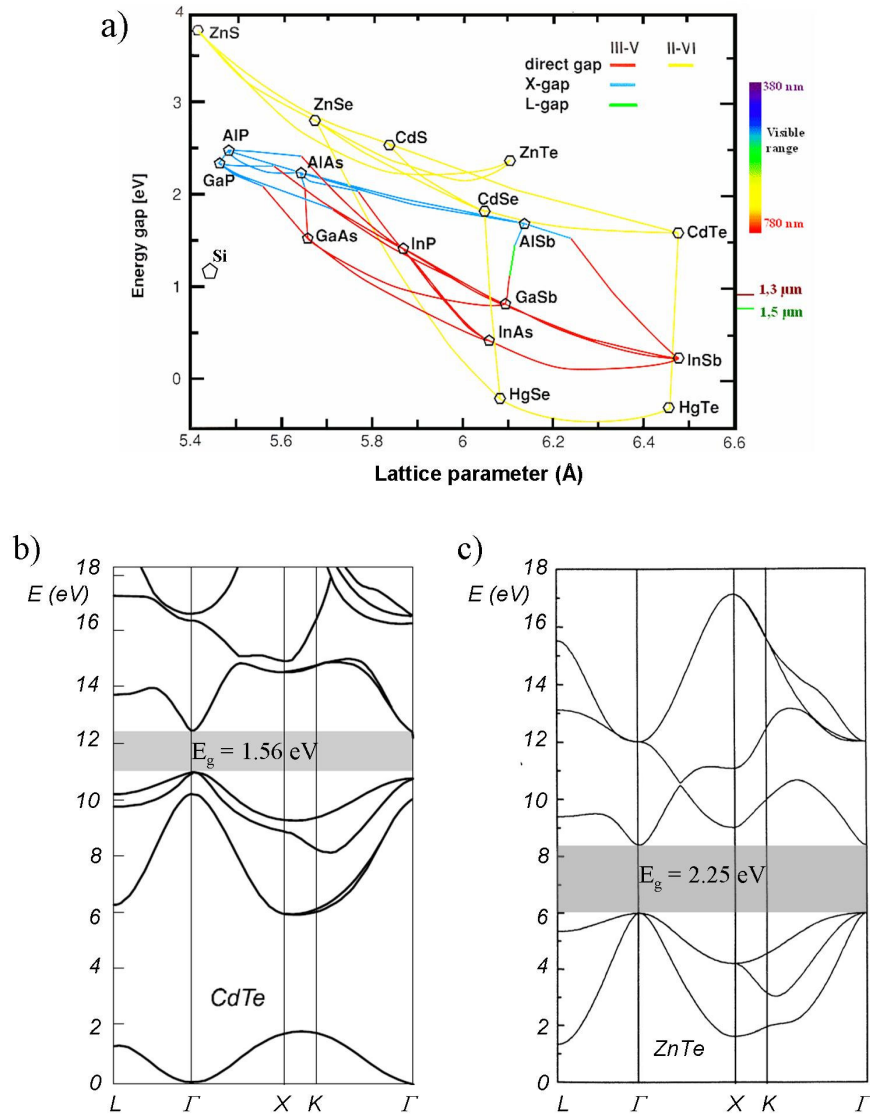


Figure II-8. a) Band gap and lattice constant of Si, III-V and II-VI semiconductors [17]; b) Band structure of CdTe [16]; c) Band structure of ZnTe [18].

II.3.B. Crystallographic structure in the real space

The zinc blende structure of CdTe and ZnTe is similar to the diamond structure: Cd (or Zn) atoms are positioned at the nodes of a face-centered cubic structure and the Te atoms occupy 4 of the 8 tetragonal sites (Figure II-9).

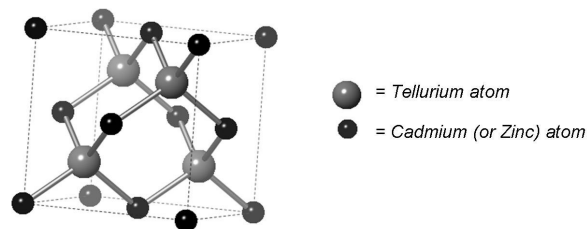


Figure II-9. Zinc blende structure of CdTe and ZnTe.

The growth of CdTe on Si(100), Si(111) or Si(211) follows a preferential orientation towards the (111) or (211) direction when the optimal growth conditions are respected (see Chapter IV for more details). So only these 2 specific orientations are described hereafter. Figure II-10a and b present respectively the (111) and (211) orientations of CdTe (or ZnTe).

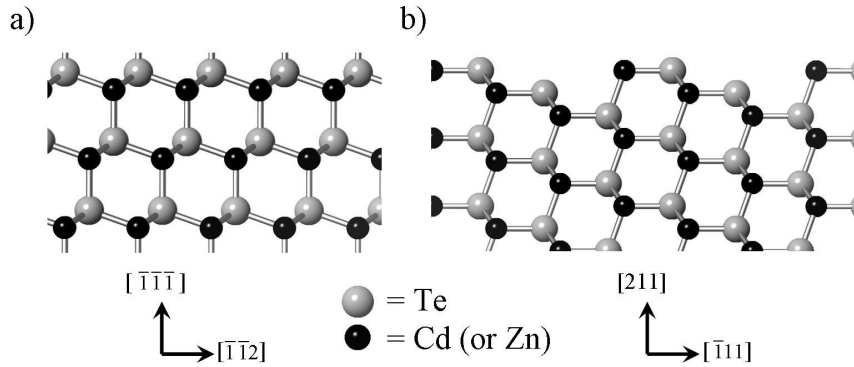


Figure II-10. a) Cd(Zn)Te (111) in the [100] direction; b) Cd(Zn)Te (211) in the [110] direction.

The Pauling electronegativities of Cd, Zn and Te are respectively of 1.69, 1.65 and 2.1, thus the CdTe (or ZnTe) surface with a (111) orientation is polar. Only two orientations are energetically favorable: CdTe(111)A which is a Cd-terminated surface and CdTe($\bar{1}\bar{1}\bar{1}$)B which is Te-terminated. These specific orientations present a top layer with atoms containing one dangling bond (Figure II-11). The two other unstable faces (CdTe(111)B and CdTe($\bar{1}\bar{1}\bar{1}$)A) present a top layer with atoms containing three dangling bonds.

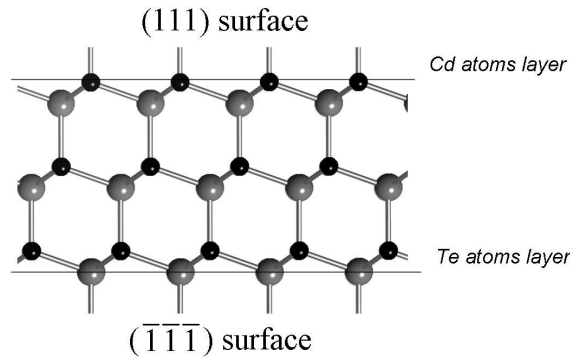


Figure II-11. Polarity of CdTe(111).

II.3.C. Crystallographic structure in the reciprocal space

The reciprocal lattice of the zinc blende structure is similar to the diamond reciprocal lattice. The difference can be found in the structure factor because the atoms in the unit cell are of different chemical species. Hence, the electronic structure is not the same, leading to different

form factors (f_j) for Cd, Zn and Te. The basic vectors (**abc**), (**a'b'c'**), (**a*b*c***) and (**a*b*c***) defined previously can always be considered. In the (**a'b'c'**) and (**a*b*c***) primitive axis systems and considering a Cd (or Zn) atom in position (0,0,0) and Te atom in ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) in the real space, the structure factor can be written as:

$$S_{hkl} = f_{Cd(or\ Zn)} + f_{Te} \cdot e^{-i2\pi\left(\frac{h'+k'+l'}{4}\right)} \quad (2.11)$$

Because of the difference between the form factor of Cd, Zn and Te, the structure factors for the zinc blende structure are different from the diamond structure case. As an example, for CdTe:

$$S_{hkl} = \begin{cases} f_{Cd} + f_{Te} & \text{if } h' + k' + l' = 4n \\ f_{Cd} - i f_{Te} & \text{if } h' + k' + l' = 4n + 1 \\ f_{Cd} + i f_{Te} & \text{if } h' + k' + l' = 4n + 3 \\ f_{Cd} - f_{Te} & \text{if } h' + k' + l' = 2(2n + 1) \end{cases} \quad (2.12)$$

These results obtained in the (**a'b'c'**) and (**a*b*c***) primitive basic vectors can be translated in the common basic vectors using the (**abc**) and (**a*b*c***) systems based on the vectors for the face-centered cubic structure, leading to the following structure factors:

$$S_{hkl} = \begin{cases} f_{Cd} + f_{Te} & \text{if } h + k + l = 4n \\ f_{Cd} - i f_{Te} & \text{if } h + k + l = 4n + 1 \\ f_{Cd} + i f_{Te} & \text{if } h + k + l = 4n + 3 \\ f_{Cd} - f_{Te} & \text{if } h + k + l = 2(2n + 1) \end{cases} \quad (2.13)$$

Hence, the major difference between the diamond and the zinc blende structures is that there is no complete extinction if the sum of the Miller indices is the double of an odd number. The only conditions leading to a complete extinction is found when the Miller indices don't have the same parity (property derived from the ideal face-centered cubic structure).

Taking into account the systematic extinctions due to the pure face-centered cubic structure, the diamond structure and the zinc blende structure, the following reciprocal lattices can be drawn in Figure II-12a and b. Only the nodes leading to an observable diffraction are represented. The blue points are associated with a strong interference between the diffracted beams, the red points account for a weaker interference and the yellow nodes represent the very weak interference (leading to completely destructive interference in the silicon case).

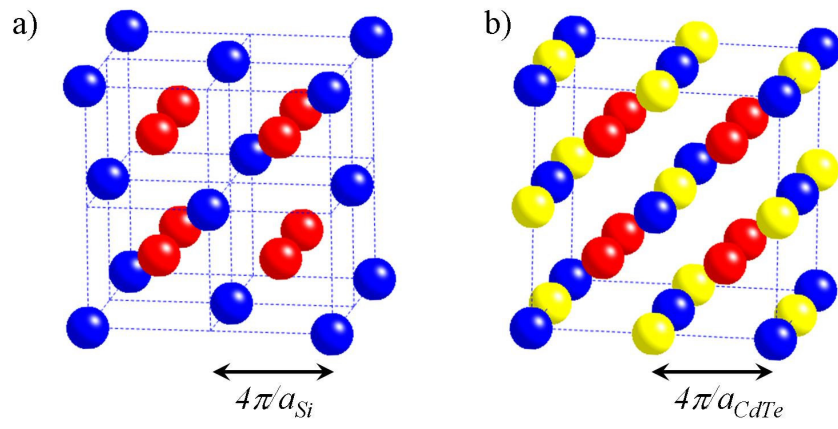


Figure II-12. a) Diamond structure reciprocal lattice and b) Zinc blende structure reciprocal lattice considering the structure factors.