1 Introduction

In 1895, Wilhelm Conrad Röntgen, the first Nobel price winner in Physics (1901), discovered the existence of unknown and invisible rays during an experiment on discharge of electrical currents in highly evacuated glass tubes [1]. He performed the experiment in darkness and noticed that an object, a barium platinocyanide-coated screen, started to luminesce in his room. The radiation responsible for this phenomenon was called X-rays. Röntgen also discovered luminescence of other materials, such as calcium sulphide or uranium glass. In addition, he found that objects placed between the X-ray source and these luminescent materials could alter the luminescence intensity and led to shadows of different intensities on a photographic film [2]. This was the beginning of X-ray imaging. One of the first X-ray images taken by Röntgen is shown in Fig. 1.1.

Nowadays, X-ray imaging is used in important applications, such as non-destructive evaluation of materials and medical imaging. As observed by Röntgen, the principle is based on the fact that materials have different X-ray absorption coefficients. For instance, at equal thicknesses, X-rays will be more easily transmitted through human tissue and paper than through bones, stones or lead. Thus, if an X-ray sensitive device is placed behind the irradiated object, which could be a human body, an image of the object can be obtained from the device. One of the most commonly used and known devices is the photographic film. The film is composed of a thick layer of plastic or paper (the base) covered with multi-layers of silver bromide crystals, acting as sensitive grains. When exposed to X-rays, these crystals become silver atoms, which later form an opaque layer of silver grains during the development. The non-exposed crystals are removed, leaving transparent zones [4]. As a result, a negative of the image is obtained. Photographic films are classified in different categories, depending on their speed and spatial resolution. These two characteristics are

![Fig. 1.1 Radiograph of the hand of Albert von Kolliker, made at the conclusion of Röntgen's lecture at the Würzburg Physical-Medical Society (1896) [3]. The ring can easily be seen.](image-url)
related to the grain size and a tradeoff has to be made since high-speed films are obtained with large grains whereas high spatial resolution is obtained with small grains. The speed corresponds inversely to the required exposure time, which defines the film sensitivity. Although images with high spatial resolution can be obtained, the use of photographic film is time consuming and requires handling of hazardous chemical products due to the development [5].

During the last decade digital X-ray imaging detectors have been developed, and a few detectors were recently introduced on the market to replace photographic films [6]. These detectors enable real time imaging but still need to be improved to reduce the X-ray dose and to enhance the picture quality, which is evaluated by the signal-to-noise ratio (SNR) and the spatial resolution. The work presented here is part of the 3D-RID European project [7] and has been motivated by dental applications where images with a SNR of 50 and a spatial resolution in the range 8-10 lp/mm at lowest possible doses are required. Three detector concepts, all based on macropore arrays, were proposed. Thus, the goal of this thesis is to develop techniques to form macropore arrays in silicon and to develop the specific technologies related to each detector design. The challenges are to form deep macropore arrays of different geometry (pitch of 50 µm with 40 µm or 10 µm large pore diameters), to process the pore walls (reflective walls and formation of photodiodes) and to fill the pores with a scintillator. As can be seen in Fig. 1.2, the function of an X-ray imaging detector is to convert the incoming X-rays into electric signals, which are then treated to obtain an image.

Two of the three detector concepts are based on detection of X-rays via a scintillating material, while the third one uses semiconductors, and particularly silicon, as a detecting material. The visible light emitted from the scintillator was detected by either a charge-coupled device (CCD) or photodiodes. Chapter 2 presents the three detector concepts. Although deep reactive ion etching was employed to form the macropore arrays, the study focussed more on silicon electrochemical etching, which is presented in chapter 3. Here, an introduction to the technique is given and formation of macropore arrays in n-type silicon is explained and illustrated. Chapter 4 presents the detector processing and characterization. The goal is not to repeat all the results reported in the appended papers but to give some highlights, complementary information and recent results. Chapter 5 gives a summary, general conclusions and outlook. The three papers related to this work are included at the end of the thesis.

Fig. 1.2 Dental X-ray imaging applications.
This picture was composed from images in Refs. 8 and 9.
2 X-ray imaging detectors

The purpose of this chapter is to introduce the three detector concepts investigated during the thesis and to give some information about the components and materials composing the detectors. The first concept is based on detection of X-rays from a scintillator, whose emitted light is then detected by a Charge Coupled Device (CCD). The second detector uses also a scintillator to detect the incoming X-rays but the photons emitted from the scintillator are detected by photodiodes instead of a CCD. The third type of detector is based on detection of X-rays from a semiconductor.

2.1. CCD-based detectors

2.1.1. CCD principle

It is “in the space of one hour on October 17, 1969, that George Smith and Willard Boyle from Bell Laboratories sketched out the CCD’s basic principle…. and outlined applications including imaging as well as memory” [10]. A CCD consists of a series of light-sensitive elements, also called pixels or photosites, arranged in a matrix of lines and columns. Each element is a MOS capacitor (metal–oxide–semiconductor) enabled to convert photons into electrical charges and to store these charges. Later, the charges are transferred from one MOS capacitor to another and finally read out at the end of the row by an amplifier. The detected time sequence of charges is later used to recompose the image. In other words, the CCD principle is based on charge carrier photogeneration, the charge storage of a MOS capacitor and the charge transfer.

Photogeneration

Incident photons of energy $E$ absorbed in a semiconductor of band gap $E_g$ can generate electron-hole pairs (EHPs) either via direct band-to-band transitions ($E > E_g$) or using forbidden gap energy levels $E_L$, from which electrons can be excited to the conduction band either thermally or by a second photon, as shown in Fig. 2.1(A). If one of these conditions is satisfied, the photon energy can be consumed to transfer one electron to an upper energy level [11]. The vacant place left by the electron is called a hole, and can be considered as a positive charge carrier. For silicon, photogeneration is effective in the range 1.1 eV - 10 keV. At wavelengths above 1.1 µm ($E < 1.1$ eV), the photon energy is not high enough to inject electrons from the valence band to the conduction band. On the other hand, at energies above 10 keV, the interaction probability between a photon and silicon becomes too low due to the low absorption coefficient of silicon at these wavelengths.
**Charge storage in a p-Si MOS capacitor**

A MOS capacitor, characterized by its threshold voltage $V_t$, constitutes the basic element of a CCD. Depending on the potential applied to the electrode (made of poly-silicon here), the MOS can operate in three regimes: accumulation, depletion or inversion. When a positive bias $V (V > V_t)$ is applied on the electrode of a p-Si MOS capacitor, the inversion regime is reached and a large depletion region (SCR) forms under the oxide (Fig. 2.1(B)). Photons impinging on the MOS go through the SiO$_2$ layer and the electrode, both transparent, and are then absorbed by silicon, where EHPs are generated. If absorption occurs in the SCR, EHPs are separated by the electric field; as a result, the holes go to the rear side of the capacitor while the electrons go to the SiO$_2$/Si interface. If absorption occurs outside the SCR, charges will either recombine (opposite effect of photogeneration) or contribute to the signal after diffusion to the SCR. The electrons will be stored under the oxide as long as a high enough positive bias is applied to the electrode. The MOS structure is usually coated by an anti-reflective layer to increase its efficiency [12].

**Charge transfer or Coupling**

The charges stored in the MOS capacitor can be transferred using different sensor architectures. In all cases, charges are transferred to a storage area, moving from one MOS capacitor to another. Each MOS capacitor usually has three electrodes whose potentials are cycled in order to move the charge packet. Electrons migrate to the electrode having a higher positive potential than the one where they are stored. Figure 2.2 illustrates a charge transfer governed by clock voltages making charges moving first vertically to a register line (clock 1, line by line), and then horizontally to the transfer pixel (clock 2). Finally, information is sent pixel by pixel to a computer via an amplifier and an Analogical/Digital converter. Considering a MOS capacitor in the $\mu$m size and a standard 15-mm wide CCD, this type of charge transfer can take relatively long time and cause smearing (pixels read last may be longer exposed). An alternative is to use two identical arrays: one detecting the light and another one, light protected, used for registration and readout of charges; this is called the frame transfer. Another technique is to place an extra line of MOS capacitors between every line of the CCD array; this is the interline transfer. The purpose of these extra capacitors is to store the charges of the closest pixel. This shortens the distance to the storage area. The disadvantage is the reduction of the CCD’s spatial resolution by about 50% due to the place taken by these extra MOS capacitors.

![Fig. 2.1 (A) Band diagram of a semiconductor illustrating the photogeneration of carriers, (B) Cross-sectional view of a p-Si MOS capacitor under illumination.](image-url)
Some limits
One of the problems in a CCD is the thermal generation of carriers, which can contribute to the signal. This portion of signal is called dark current or noise, and can be reduced by cooling down the CCD. Another problem is the presence of interface states that can trap the carriers at the SiO₂/Si interface, and that do not release them during the charge transfer. Loss of charges during the coupling process is called fading. Even if the charge transfer efficiency (CTE) from one MOS to another is high, the average CTE for the whole array can get quite low for a CCD containing millions of MOS capacitors. Another negative effect is the blooming, which occurs when the maximum number of electrons that can be stored in one pixel is reached. Some of the photogenerated charges may leak to adjacent pixels. Finally, it is worth noting that silicon CCDs are sensitive to light in the range 400-1100 nm with a peak around 530 nm, and that they are less sensitive to X-rays due to the poor absorption coefficient of silicon at these energies. Consequently, CCDs are combined with scintillators emitting visible light in order to be used in X-ray imaging applications.

2.1.2. Scintillators - CsI(Tl) and CsI(Na)

A scintillator is a medium that emits photons of energy $E_1$ when exposed to ionizing radiation of energy $E_2$. For instance, CsI(Tl) emits green light when exposed to X-rays. The general requirements for a scintillator are:

- high atomic number and density (related to the stopping power)
- transparent to their own light wavelength
- high light yield (usually expressed as photons/MeV)
- good energy resolution
- stability against moisture, mechanical, temperature and radiation effects.

There are two main groups of scintillators: organic and inorganic. Only inorganic scintillators and particularly Cesium Iodide (CsI) doped with Thallium (Tl) and doped with Sodium (Na) will be presented here, as these are the scintillators we employed. The dopant, also called activator, is usually written in brackets. The origin of luminescence in CsI crystals is not completely established yet [13, 14, 15]. Experimentally, CsI(Tl) presents two radiation peaks at 2.55 and 2.25 eV while CsI(Na) emits at 2.98 eV.
Growth of CsI

The techniques used to produce CsI are vapor deposition [16] and crystal growth from the melt [17]. The challenge in growing scintillators such as CsI is to maintain a uniform dopant concentration in the crystal, which is essential for an optimal light emission efficiency [16]. Vapor deposition is performed with a “two boat evaporator system” where two sources, containing respectively CsI and TlI₂, are operated at different temperatures according to the desired composition ratio of Tl into CsI. The thickness of the CsI layer reported in Ref. 16 ranges from 65 to 220 µm, but thicker layers can now be grown. If the evaporation is performed onto a patterned substrate, CsI columns of several microns diameter can be grown perpendicularly to the substrate surface [18] (Fig. 2.3). Large volumes of CsI are commonly grown from the melt using either Kiropoulos (extension of the well-known Czochralski technique) or Stockbarger techniques. The former consists of pulling the crystal from the melt, starting the crystallization with a seed to orient the growth. The later uses furnaces where a crucible containing the charge is first melted and then cooled down. The cooling rate is a crucial parameter to control and ranges typically from 20°C/h [19] to 70°C/h [20]. The dopant is directly introduced in the melt and segregation phenomena of Tl in large crystals can be avoided using the zone leveling technique where a molten zone is passed repeatedly one way and then the other way along the crystal.

![Fig. 2.3 Columnar CsI(Tl) produced by AST (Applied Scintillation Technology) [18]. Proper evaporation conditions allows growth of dense array of fine CsI needles (10 to 20 µm in diameter).](image)

Characteristics of CsI

CsI has a CsCl crystal structure and the incorporation of impurities, such as Tl and Na, into the crystal is mainly limited by its geometrical structure [19, 21, 22]. According to most of the publications found, the amount of Tl needed to obtain a high light yield efficiency should not be less than 4×10⁻² mole %. The initial powder of CsI(Tl) used in our work contained 1000 ppm, respectively 1×10⁻¹ mole %. The general features of CsI(Tl) and CsI(Na) are presented in Table 1.

| Table 1. Basic characteristics of CsI(Tl) and CsI(Na) scintillators. |
|-----------------|-----|---|-------------|-----|---|
| Material       | λ   | Z | d   | Hygroscopy | n   | Y  |
| CsI(Na)        | 420 | 54| 4.51| Yes         | 1.74|150000 |
| CsI(Tl)        | 550 | 54| 4.51| Yes         | 1.74|60000  |
2.1.3. CCD-based detector concept

Since silicon is considerably more sensitive to visible light than to X-rays, X-ray sensitive devices can be obtained by coating a Si-based CCD with a scintillator. Typically, a 250 µm thick CsI layer will absorb 80% of incoming X-rays of a standard dental X-ray source. The emission wavelength of the scintillator should be suitable to the silicon CCD. CsI(Tl) is a good candidate since it emits at a wavelength of 550 nm. The principle of such detector is illustrated in Fig. 2.4(A). X-rays striking the detector are first absorbed in the scintillator, generating secondary photons that are then detected in a silicon CCD. The main drawback of this detector concept is the loss of the CCD’s high spatial resolution due to light spreading in the scintillator [23]. An alternative is to use columnar CsI(Tl), as shown in Fig. 2.3, where the generated photons propagate along the CsI needles, thus reducing light spreading. The major problem is the tendency for the columns to widen or spread near the top. In this thesis, the investigated concept is a CCD coated with an array of scintillating waveguides where each waveguide matches a CCD pixel [24, 25]. The array is formed by filling a silicon macropore array with CsI(Tl) or CsI(Na). Each pore works as a waveguide for the photons emitted from CsI(Tl), due to reflection from the pore walls (Fig. 2.4(B)). Results obtained with detectors based on this concept are presented in section 4.1 and in appended paper A.

Fig. 2.4 CCD-based detectors: (A) Scintillator coated CCD, (B) CCD covered with a matrix of CsI(Tl) columns.
2.2. CsI-photodiode structure

2.2.1. Photodiode principle

A photodiode is a light sensitive device, which is basically a p-n junction operated under reverse bias [11, 12]. It is composed of an n-type substrate and a p-type (boron doped) region located at the surface. A space charge region (SCR) forms at the p-n interface under reverse conditions. When photons strike the diode, EHPs are generated in the substrate (see photogeneration in part 2.1.1). If EHPs are created in the SCR, electrons and holes are separated by the electric field, and then diffuse to the contacts to finally create a signal in the external circuit. On the other hand, if EHPs are created in the neutral n or p-type regions, carriers may recombine. However, if EHPs are generated in the neutral regions at less than a diffusion length from the SCR, they can diffuse into the SCR and be accelerated by the electric field. The current created is called photocurrent and is relatively small as compared to the forward current of the p-n diode but is significantly higher than the reverse current of the diode in the darkness. This explains why a photodiode operates under reverse bias.

The geometrical characteristics and doping levels of the photodiode are critical and control its efficiency and response speed. The efficiency of a photodiode depends on the size of the SCR. A large SCR is preferable for effective light absorption. The SCR width W of a p-n junction is expressed as:

\[
W = \sqrt{\frac{2 \times \varepsilon_{SC} \times \varepsilon_{o} \times \left( \frac{1}{N_A} + \frac{1}{N_D} \right)}{q} \times (V_{bi} - V)}
\]

(Eq. 2.1)

where \( q = 1.6 \times 10^{-19} \) C, \( V \) is the applied bias, \( V_{bi} \) is the built-in potential in the diode (in the order of 0.6 V for a silicon diode), \( \varepsilon_{SC} \times \varepsilon_{o} \) is the permittivity (\( \varepsilon_{Silicon} \times \varepsilon_{o} = 11.9 \times 8.85 \times 10^{-12} = 1.053 \times 10^{-10} \) F/m), \( N_D \) and \( N_A \) are the doping levels in the n and p-type regions, respectively.

A low doping of the n-region, as compared to that of the p-region, will induce a large depletion region. Therefore, the efficiency of the photodiode can be increased using a very low doped region (almost intrinsic) between the p+ layer and the n+ region (needed for the backside contact); it is called a pin diode (Fig. 2.5). On the other hand, for high response speed, a thin SCR is needed in order to reduce the transit time of carriers. Thus, there is a tradeoff on the SCR width between high efficiency and optimal response time. It is also
necessary to have thin p+ and n+ layers in order to reduce absorption in these regions. The spectral response of a silicon photodiode is shown in Fig. 2.6(A). Maximum detection efficiency is observed around 875 nm. The dependence of the reverse current on light intensity is illustrated in Fig. 2.6(B).

![Spectral response of a silicon photodiode](image)

Fig. 2.6 (A) Spectral response of a silicon photodiode [26], (B) Dependence of the photodiode reverse current on light intensity.

2.2.2. Detector concept

This detector concept also uses an array of macropores filled with CsI(Tl) to detect the incoming X-ray photons. However, it differs from the previous detector concept since the photons emitted from the scintillator are not detected by a CCD at the bottom of the pores but by photodiodes formed in the walls of the silicon pores. This is a considerable change both for the fabrication and for the charge collection efficiency of the detector. In the CCD concept photons had to be directed along the pore depth towards the CCD pixels, while here photons are detected very close to where they are generated. Figure 2.7 illustrates the detection principle of such a detector. X-rays go through the top silicon layer and reach the CsI(Tl) where they are absorbed. CsI(Tl) emits photons at a wavelength of 550 nm, which are then captured by photodiodes located in the walls of the silicon pores. Compared with the CCD-based detector, the challenging steps in the detector fabrication are the formation of p-n junctions in the pore walls and their contacts. The electrical signal, i.e. the accumulated charge in each pixel, then needs to be readout by a special read-out-chip in proximity with the CsI-photodiode structure (normally bump-bonded). In this thesis work, the formation of p-n junctions in the pore walls was studied and the results are presented in section 4.2 and in appended paper B.

![Detector concept diagram](image)

Fig. 2.7 Principle of the CsI-photodiode detector [Appended paper B].
2.3. Semiconductor-based detectors

2.3.1. Semiconductors in X-ray imaging

Semiconductors can also be used as detecting materials in X-ray imaging sensors. Figure 2.8(A) shows a relatively simple planar detector, which consists of a p-n junction operating under reverse bias [7]. The EHPs created in the semiconductor under X-ray exposure are separated by the electric field of the SCR, and are then collected by electrodes placed on the front and the back sides of the semiconductor. The potentials applied to the electrodes serve to deplete the semiconductor, ideally on all its thickness. Several semiconductors can be used to detect X-rays. The properties of some of them are given in Table 2. The main feature is the absorption length required to absorb the incoming X-rays. High atomic number (Z) and density (d) values are needed for a high stopping power. The mass absorption coefficients used to calculate the absorption lengths presented in Table 2 were taken from Ref. 27. Another aspect, which is also an important selection factor, is the status of the material technology. It should be possible to grow high quality crystals (high purity, high resistivity) and a technology to process the material should be available. Indeed, despite its poor stopping power, silicon still has the most advanced technology, making it a good candidate. Competitors of silicon, such as GaAs, CdTe (or even CdZnTe) and SiC, still suffer from their poor crystal quality and processing technology. However, the growth of these materials is currently under development and recent advances on the crystal quality of GaAs, for instance, have been reported [28]. Another material that may be used in X-ray imaging is lead iodide (PbI₂), which presents promising properties [29, 30].

Table 2. Characteristics of some semiconductors used for X-ray imaging.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>GaAs</th>
<th>CdTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number Z</td>
<td>14</td>
<td>Z₉₃ = 31</td>
<td>Z₉₄ = 48</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.3</td>
<td>5.3</td>
<td>5.8-6.06</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>1.12</td>
<td>1.43</td>
<td>1.5</td>
</tr>
<tr>
<td>Absorption length (µm) at 30 keV (80% of absorption)</td>
<td>~5000</td>
<td>~220</td>
<td>~125</td>
</tr>
</tbody>
</table>

2.3.2. Detector concept

One of the drawbacks in the planar detector concept is the high voltage required to deplete the entire semiconductor thickness, which is in the order of 200 V for a 200-µm thick silicon detector. Furthermore, due to the damages created in the material during X-ray exposure, a potential of 2000 V would be required to deplete the same 200-µm thick planar detector after 10 years of use. The bias needed to fully deplete the detector is proportional to the square of the distance between the electrodes (see Eq. 2.1), and the collection time is proportional to the distance. Thus, new detector designs have to be considered to reduce the distance between the electrodes. The detector concept studied here was first presented by Parker et al. in Ref. 31 and was called “three-dimensional” (3D) detector. It consists of a silicon pore array having electrodes in each pore, as shown in Fig. 2.8(B). The EHPs generated in the semiconductor under X-ray radiation are separated by the electric field and collected at the electrodes made in the pores. This reduces significantly the distance between the electrodes without reducing the detector sensitivity. Consequently, after 10 years of operation, a 200-µm thick 3D detector with 20 microns spacing would only require 20 volts and not 2000 V as it is predicted for a 200-µm thick planar detector [7]. In previous concepts
(Chapters 2.1 and 2.2), both large and deep holes were needed in order to get highly sensitive detector (for a large area and volume of scintillator). In this concept, very deep and narrow holes should be made for an optimal active area and volume. The spacing between the pores determines the spatial resolution of the detector. The challenging processes in the fabrication of a 3D detector are the formation of deep and narrow holes in the semiconductor, the formation of electrodes in the pores and the formation of contacts to the electrodes. In this thesis, the formation of narrow pores in silicon by electrochemical etching was studied and the results are presented in section 4.3.

Fig. 2.8 Schematic of semiconductor-based detectors: (A) planar detector, (B) three-dimensional detector.
3 Silicon electrochemical etching

3.1. Porous and electropolished silicon

Studies on silicon electrochemical etching already started in the fifties (Uhlir and Turner), and it is in 1958 that one of the first papers reported electropolishing of silicon by anodic etching in hydrofluoric (HF) acid solutions [32]. It was also observed that, depending on the experimental parameters, a black layer could form on the silicon surface. It was later recognized as a layer of randomly distributed and interconnected pores, namely porous silicon. The pores trap incident light, resulting in the black appearance. Figure 3.1 shows SEM images of both porous and electropolished silicon viewed from the top. Furthermore, an intermediate regime, also called transition regime and characterized by the formation of pillar-like structures, can be observed. Depending on the pore size, porous silicon is classified in three categories: micropore (< 2 nm), mesopore (2-50 nm) and macropore (> 50 nm) as in Fig. 3.1 [33]. In the following text, the etched face of the silicon substrate (in contact with the HF solution) will be called the front side, whereas the opposite face, the back side.

3.1.1. Chemical reactions and valence number

The chemical reaction between the HF solution (also called electrolyte later) and silicon does not only involve the species of the electrolyte and silicon atoms but also holes (h⁺, positive charge carriers). Indeed, a charge transfer is needed at the silicon/electrolyte interface for the chemical reaction to occur. Electrochemical etching of silicon is possible for both p-type and n-type silicon. The difference is that h⁺ are the majority carriers in p-type silicon [34] while they are the minority carriers in n-type silicon. Thus, h⁺ have to be generated by external means in n-type silicon. The most common way is photogeneration (see
section 2.1.1). An alternative is to inject the minority carriers from a p-n junction formed at the back side of the wafer [Appended paper C]. In addition, etching of low-resistivity n-type silicon can occur due to electrical breakdown [35]. The two situations studied in this thesis were photogeneration and \( h^+ \) injection from a p-n junction. These two techniques will be presented in parallel. Although there is still discussion on the actual chemical reactions, it is at least rather clear that silicon dissolution can happen under two different pathways, leading either to porous silicon or to electropolished silicon. It is also rather well established that porous silicon is formed by consuming two electrical carriers (holes) to dissolve one silicon atom whereas polished surfaces require four carriers. The number of electrical carriers exchanged during the dissolution of one silicon atom is called \( n \), the valence number. These carriers can either be \( h^+ \) coming from the silicon bulk and consumed in the reaction, or electron injected from the solution into the bulk. As a result, a current passes through the sample and the solution during etching. The valence number \( n \) can be calculated by measuring the mass of dissolved silicon as shown in expression (Eq. 3.1), or by measuring the etched depth in the case of an electropolished sample (Eq. 3.2):

\[
n = \frac{I \times t}{q \times \frac{\Delta m}{d_s} \times N_{Si}} \quad \text{(Eq. 3.1)} \quad \text{or} \quad n = 1.25 \times \frac{J}{d} \Delta d \quad \text{(Eq. 3.2)}
\]

where \( I \) is the current (A), \( J \) is the current density (A/cm\(^2\)), \( t \) is the etch time (s), \( \Delta m \) is the dissolved mass of Si (mg), \( \Delta d \) is the etched depth (\( \mu \)m), \( q = 1.6 \times 10^{-19} \) C, \( d_{si} = 2330 \) mg/cm\(^3\) and \( N_{si} = 5 \times 10^{22} \) at/cm\(^3\). The current, the etch time, the dissolved mass and the etched depth are measured experimentally.

Figure 3.2 is a representation of a chemical dissolution reaction that could occur during electrochemical etching of silicon in HF. The initial silicon surface is hydrogen-terminated, as was shown to be the case in HF [36]. The reaction first occurs between Si atoms and \( F^- \) ions, involving only two charge carriers to form SiF\(_2\). SiF\(_2\) is then dissolved by HF molecules of the solution, forming SiF\(_4\); this is a divalent reaction [36, 37]. Later, SiF\(_4\) is dissolved in the solution to become a form of the stable product H\(_2\)SiF\(_6\).

![Fig. 3.2 Divalent chemical dissolution reaction of silicon in HF solution [37].](image)

The second possible reaction, the tetravalent reaction – involving 4 carriers - could start similarly as in Fig. 3.2, but instead SiF\(_2\) is dissolved using two more charge carriers to
break the two last silicon back-bonds. Another tetravalent reaction possibly responsible for silicon electropolishing is: (1) formation of an oxide due to OH⁻ ions, (2) dissolution of the oxide in HF [36]. However, other reaction mechanisms have been proposed [see Ref. 37 for a review]. The difficulty in finding the reaction mechanisms can be explained by the number of species contained in the aqueous HF solution: HF, (HF)₂, (HF)₂⁻, F⁻, OH⁻, H₂O, H₃O⁺, and maybe other complexes.

3.1.2. Experimental setup

Two setups were used during this work. A sketch of the recently installed experimental setup is shown in Fig. 3.3. The light source is located at the backside of the sample, which is usually the case for macropore formation [38, 39, 40]; however, for other purposes the front side of the sample can be illuminated as well [41]. The cell is made of PVC, which is resistant to HF. Two Platinum electrodes are mounted. However, all voltages given in this chapter refer to the bias between the counter electrode and the sample back side. There is a voltage drop of about 0.7 V between the counter electrode and the reference electrode (recently installed). A sapphire window allows observation of the sample surface during etching and possible illumination of the sample front side. The reaction mechanisms between silicon and HF have been introduced in section 3.1.1 but not the electrochemical etching principle. Only the case of n-type silicon is discussed since it was the material used in this work. First, EHPs are generated in the silicon bulk using a light source (300 W or 20 W halogen lamp). A positive bias \( V \), with respect to the solution potential, is applied to the sample back side. Drift-diffusion of \( h^+ \) through the sample thickness (525 \( \mu \)m) allows chemical reactions at the electrolyte/silicon interface. Charge transfer happens and a current \( I \) is measured. Etching was also performed using \( h^+ \) injection from a p-n junction. The lamp was of course not used in this case, making the setup simpler. It also avoids the sample and the solution to warm up, as it can be the case with a lamp. Indeed, a shield with a hole matching the back side window was placed between the lamp and the sample to reduce heating.

HF solutions of different concentrations were used, composed of 300 ml of di-ionised water, 100 ml of ethanol (used as a wetting agent) and a volume \( V_{HF50\%} \) of HF50%. The HF concentration “c”, in percentage of weight (wt%), was calculated as follows (Eq. 3.3 with \( V_{HF50\%} \) in liter):
The other parameters that influence etching and macropore formation are:

- The light intensity, determining the number of generated holes in the bulk (cf. next section). The light wavelength is also an important parameter but was not studied here.
- The properties of the silicon substrate: resistivity, orientation and type.
- The temperature
- The applied bias
- The etching current density

Some of these parameters have been studied and results are presented in next sections. In order to apply a uniform potential to the sample, an Al grid was formed at the back side of the sample prior to anodic etching. This was only done for high resistivity wafers (typically larger than 20-40 Ωcm).

3.1.3. JV characteristics - Influence of the HF and h⁺ concentrations

Figure 3.4 shows a typical JV characteristic (current density – voltage) for an n-type silicon sample using a 1.5 wt% HF solution. The first peak of these curves is usually called $J_{ps}$ and, according to Ref. 33, corresponds to the critical polishing current density. Three different regimes are observed: porous silicon formation ($J < J_{ps}$), transition regime ($J \approx J_{ps}$) and electropolishing regime ($J > J_{ps}$) [33, 42]. In other words, a low anodic bias leads to porous silicon formation while a high bias leads to electropolished silicon. In fact, the concentration of F⁻ ions, which can be subject to electric fields, most likely becomes higher than the concentration of HF molecules at the silicon/electrolyte interface for high bias. Thus, referring to the chemical reactions previously presented, electropolishing is favored.

![Fig. 3.4 Typical JV characteristics for n-type silicon, using different Lamp/sample distances “L”.

$$c = \left( \frac{1}{2} \times V_{H_2O} \times \rho_{H_2O} + V_{\text{ethanol}} \times \rho_{\text{ethanol}} + V_{HF50\%} \times \rho_{HF50\%} \right) \times 100$$

(Eq. 3.3)

$$c = \left( \frac{1}{2} \times 0.3 \times 1 + 0.1 \times 0.79 + V_{HF50\%} \times 1.16 \right) \times 100$$
As can be seen in Fig. 3.4, the maximum current that can be reached increases with light intensity. The current is both dependent on the applied bias and on the light intensity, which gives two ways to control it. The bias can be set independently from the current. The lamp used was a 300 W halogen lamp and was placed at different distances ("L") from the sample. Higher currents are measured for a short lamp/sample distance since the concentration of h+ generated in the bulk becomes higher. A similar dependence is observed with the HF concentration. Higher HF concentrations allow to obtain higher etching currents. The dependence of the etching currents on the HF concentration is shown in Fig. 3.5 for both photogeneration of carriers and injection of carriers from a p-n junction. The first peak of the J-V curve (J=Jps) decreases with decreasing HF concentration. Thus, the electropolishing regime should be easier to reach for low HF concentration (requiring lower current). These experiments show that the reaction can be limited by the number of h+ or the number of HF molecules available at the silicon/electrolyte interface.

A series of experiments was performed to calculate the valence numbers, using carrier injection from a p-n junction and a 2.2 wt% HF solution. The data are given in Table 1 of appended paper C, and are also presented in Fig. 3.6. The n values were calculated according to expressions 3.1 and 3.2, and vary between 2 and 4, as expected [33]. The value is close to 2 when porous silicon is formed and close to 4 when the surface is electropolished. Scanning electron microscopy (SEM) and optical microscopy was used to observe the sample structure. In this case, the critical polishing current is about 8 mA/cm², which is rather close to the calculated value of Jps (∼ 10 mA/cm²) from the empirical expression given by Lehman [33]:

\[
J_{ps} = Cc^{3/2} \times \exp\left(-\frac{E_a}{kT}\right) \quad (\text{Eq. 3.4})
\]

where c is the HF concentration (in wt%), T the temperature (in Kelvin), \(k = 1.38 \times 10^{-23}\) J/K, \(C = 3300\) A/cm² (a constant), and \(E_a = 0.345\) eV. Note the high sensitivity to thermal variation indicated by this formula: a 10°C raise in temperature results in a 54% higher \(J_{ps}\).

This experiment, together with the J-V characteristics presented earlier, shows that electrochemical etching using carrier injection from a p-n junction or photogeneration behaves...
similarly. Also, current values obtained at a given HF concentration are in the same range, confirming the viability of carrier injection from a p-n junction.

3.1.4. Hole injection from a p-n junction: comments

The p-n junctions were made in high-resistivity (3.8-5.5 kΩ cm) n-type silicon substrates by boron diffusion from a solid source (boron wafers) at 1150°C for 105 min, resulting in a 6 µm thick p⁺ layer with a maximum B concentration of 2×10²⁰ cm⁻³. The process flow is presented in Fig. 3.7. During anodic etching, the diode is under forward bias and h⁺ are injected from the p⁺ side of the junction into the valence band of the n⁻ side. These carriers will either recombine with electrons (e⁻) in the bulk or diffuse towards the silicon/electrolyte interface to participate in the dissolution reaction. Electrons injected from the n⁻ side into the p⁺ side of the junction, together with e⁻ recombined in the bulk, call for an e⁻ supply. These e⁻ could be injected from negative ions of the electrolyte into the conduction band of silicon. This hypothesis has not been demonstrated yet but such a phenomenon has already been suggested elsewhere [36]. Note that this e⁻ injection from the electrolyte may not be needed (or may be smaller) in the case of photo-electrochemical etching since both h⁺ and e⁻ are generated in the bulk [Appended paper C].

Extension of this technique to n-type silicon of lower resistivity (20-40 Ω cm) has not been successful when diodes were formed by boron diffusion. The high temperature process used (1150°C) may lower the lifetime of the minority carriers in the bulk, limiting the reaction and therefore reducing the achievable current density. A similar observation was made in the case of photo-electrochemical etching for 20-40 Ω cm samples that had been oxidised at high temperatures. The current densities were much lower after than before oxidation. However, it worked when p-n junctions were formed on top of a 20-40 Ω cm n-type substrate using epitaxy of boron doped silicon around 600°C. Significant current densities, in the range of 25 mA/cm² for a 4.2 wt% HF solution, were measured. This proves that the carrier lifetime was still sufficiently high. In conclusion, high temperature processes such as diffusion or implantation followed by annealing cannot be used for low resistivity n-type silicon, limiting the technique to some extent.
3.2. Macropore arrays in n-type silicon

Macropore arrays can be formed by electrochemical etching if the front side of the silicon wafer is patterned [33, 38]. Only large macropores of diameter in the range 20-40 µm will be presented in this section. These pores are designed to be used in detectors using scintillators as a detecting material where large pores and thin walls are preferable for large active area and volume. The formation of thinner pores will be presented in section 4.3 but the mechanism is the same. All samples presented in this section had a high resistivity in the range 2-5.5 kΩcm (n-type). A 300 W halogen lamp was used.

3.2.1. Formation mechanism

The silicon wafer has to be processed on both front and back sides prior to electrochemical etching, where specifically a front side lithographic step defines the macropore pitch (repetition rate). First, inverted pyramids are formed at the front side of the silicon wafer by anisotropic KOH etching. Indeed, in warm KOH solution (for instance 80°C, 30 wt% KOH, 1 µm/min), the (100)-oriented silicon planes are etched faster than the (111)-oriented ones. SiO₂ or nitride can be used as a mask. These pits are used to initiate the pore growth during the subsequent anodic etching. As explained earlier, two types of carrier generation are possible: a light source or a p-n junction. The two process flows are shown in Fig. 3.7. While etching the SiO₂ layer of one face, the SiO₂ layer of the other face had sometimes to be protected for subsequent use (front side: fsp, back side: bsp).

![Fig. 3.7 Process flows for photogeneration and carrier injection from a p-n junction](image)
In contact with HF and under anodic bias, a space charge region (SCR) forms in n-type silicon. The \( h^+ \) created at the sample back side will either recombine in the bulk, or drift-diffuse to the silicon/electrolyte interface (see Fig. 3.8). If not recombined, \( h^+ \) are accelerated towards the top of the pyramids by the electric field of the SCR. The current lines are then bent to the pore tips, where \( h^+ \) participate in the chemical reaction. The passivation of the pore walls is therefore due to the SCR, free of carriers \([33, 38]\).

The resistivity of the sample is of great importance since the SCR width of a junction depends on the doping level. High resistivity wafers results in large SCR and vice versa (cf. Eq. 2.1). Since the SCR passivates the pore wall, high resistivity samples are required for large wall thickness (or large pore spacing). Ideally, the pore spacing should be less than two times the SCR width; however, larger spacing is possible \([43]\). Generally, it is observed that pores grown in high resistivity wafers are large and vice versa \([40]\). Thus, a compromise has to be made on the wafer resistivity if one wants to form narrow pores with a large spacing. It is also crucial to have a uniform pattern on the front side surface since the current lines are very dependent on the pit positions. A non-uniform pattern would lead to a “dying” of pores and non-homogeneous pore shapes. The orientation of the silicon substrate is also of interest since pores grow preferentially along the (100) directions \([43]\). Thus, pores grow perpendicularly to the surface in an (100)-oriented substrate but not in an (111)-oriented one. According to Lehmann, the condition at the pore tip is that the current density is equal to the polishing current density \((J_{tip} = J_{pol})\). Thus, for a given pattern (pitch), an increase of the total current density will result in larger pores. This condition implies that the pore bottom is always polished and pores with very smooth walls can be obtained.

![Fig. 3.8 Formation mechanism of macropores in n-type silicon using photogeneration. Arrows show the current lines.](image)

3.2.2. Macropores formed by photoelectrochemical etching - Growth rate

A quadratic repartition of the pores was used to fabricate the arrays. Figure 3.9 shows cross sections of samples having a pitch of 45 \( \mu m \) before and after etching. The two samples shown in Fig. 3.9 were etched under similar conditions except for the current density and the etch time. Clearly, the sample etched for a longer period of time has deeper pores: 230 \( \mu m \) (Fig. 3.9C) and 165 \( \mu m \) (Fig. 3.9B). The higher current density used in the case C led to more electropolishing, which explains the flat pore bottoms and the thinner walls than in the case B.
Indeed, the pore diameter is dependent on the current density. This point will be discussed again in section 4.3.

### Parameters
- Pore spacing: 45 µm, 4.2 wt% HF, 1.5 V
- 300 W halogen lamp at L = 4.5 cm
- (B): J = 15 mA/cm², t = 3.5 hours.
- (C): J = 17.5 mA/cm², t = 6 hours.

---

**Fig. 3.9** SEM images of (A) initial pits and (B, C) macropores formed under stable conditions.

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**Fig. 3.10** (A) Pits formed by KOH etching, (B) Macropores after electrochemical etching.

**Parameters:**
- c = 4.2 wt%, L = 5 cm, 1.5 V, J = 17.5 mA/cm², t = 6 hours.
**Geometry:**
- Pore depth: 230 µm, spacing: 30 µm, wall: 3 µm.

A sample with a spacing of 30 µm is shown in Fig. 3.10. The etch rate is about 0.64 µm/min, which is a typical etch rate for macropore formation. However, different HF concentrations and current densities have been tested. Based on the result of Fig. 3.10, expression (Eq. 3.4) can be used to estimate the current density to be used for another HF concentration. Indeed, if one considers that the correct parameters have been found for an HF concentration $c = c_1$ and a current density $J = J_1$, the current density to be used with an HF concentration $c = c_2$ can be estimated according to:

$$J_2 = J_1 \times \left(\frac{c_2}{c_1}\right)^{3/2} \quad \text{(Eq. 3.5)}$$
Figures 3.11 and 3.12 show two examples where the proportionality in $c^{3/2}$ is almost respected. The experimental parameters were similar to those given for the sample in Fig. 3.10, except the etching time, the HF concentration and the current density. These parameters are written in the figure captions. Considering that the sample in Fig. 3.10 was etched under stable condition and according to (Eq. 3.5), the current densities to be used to etch samples in Fig. 3.11 and in Fig. 3.12 would be 25.8 mA/cm$^2$ and 34.7 mA/cm$^2$, respectively. These estimated current densities are slightly higher than the experimental ones. This could thus explain why the sample in Fig. 3.11 presents thicker walls than the sample in Fig. 3.10, and why sample in Fig. 3.12 has small pillars at the bottom of the pores, as can be seen in the inset enlargement. Indeed, the current densities were not high enough to properly polish the pore bottoms. Nevertheless, it is interesting to note that the pore growth rate is much higher for the sample in Fig. 3.12 than for the sample in Fig. 3.10, respectively 1.23 µm/min and 0.64 µm/min. Although one could think that the HF concentration (and proportionally the current density) should be increased in order to increase the etch rate, this may not always be possible. $J_{ps}$ is indeed set by the HF concentration (Eq. 3.4) but the $h^+$ concentration should be high enough to reach this value. At some point, the light source may not be strong enough to reach $J_{ps}$. The two samples of Figs. 3.11 and 3.12 also show that extremely deep pores can be etched. In principle, pores could be grown through the whole wafer thickness. This is not allowed for experimental reasons as the electrolyte would then break through to the back side of the sample.

The growth rate as a function of the pore depth for several HF concentration and current density combinations is presented in Fig. 3.13. As can be seen, the growth rate is not constant for etching with a 5.45 wt% HF solution at a current density of 22.5 mA/cm$^2$. Etching goes much faster at the beginning than at the end of the pore growth. Most probably, the concentration of F- ions, subject to diffusion and migration, becomes higher at the pore bottom than the concentration of HF molecule, diffusion dependent. Thus, the tetravalent reaction is more likely to occur, diminishing the etch rate. Nevertheless, for a 4.2 wt% HF solution and a current density of 17.5 mA/cm$^2$, this trend is not seen and the growth rate seems to be constant. However, the range of pore depths studied at this concentration should perhaps be extended. Apparently, an increase of the current density at a given HF concentration does not increase the growth rate significantly. The conclusion is that the pore growth rate is very sensitive to the HF concentration/current density combination used. The
growth rate was increased by a factor of roughly 2 for an increase of the HF concentration from 4.2 wt% to 6.63 wt%. This gain in time should of course not be detrimental for the pore quality and the parameters should be chosen to ensure smooth pore walls.

![Growth rate versus pore depth for different HF concentration / current density combinations.](image)

**Fig. 3.13** Growth rate versus pore depth for different HF concentration / current density combinations. 
Growth rate = (Pore depth) / (Total Etching time)

### 3.2.3. Macropores formed by h⁺ injection from a p-n junction

Macropores have also been formed using injection of h⁺ from a p-n junction. Figure 3.14 and 3.15 show examples of pores with a spacing of 30 µm. A closer look along the 1.6-cm wide cross section of the sample in Fig. 3.14 revealed a pore diameter of 26 ± 1 µm and a pore depth of 167 ± 13 µm, which represents a relatively good homogeneity. The hole diffusion length is therefore homogeneous and must be larger than the wafer thickness. The etch rates for samples in Figs. 3.14 and 3.15 are respectively 0.46 µm/min and 0.54 µm/min, which is slightly slower than that measured for photo-electrochemical etching using the same conditions. Similarly, the currents used to form these structures had to be lower than that used for photo-electrochemical etching, which may be due to the temperature. Indeed, the use of a halogen lamp to generate the h⁺ heats the sample and the solution, leading to higher $J_{ps}$ as expressed in (Eq. 3.4). These two examples also show the effect of the current density on the wall thickness and, as a consequence, on the pore diameter. A macropore array with a spacing of 45 µm is shown in Fig. 3.16.
Fig. 3.14 Macropore array formed in silicon by h^+ injection from a pn junction.

**Parameters:**
- c = 4.2 wt%, J = 10 mA/cm², t = 6 hours.

**Geometry:**
- Pore depth: 167 µm, spacing: 30 µm, wall: 6-7 µm.

---

Fig. 3.15 Macropore formed array formed in silicon by h^+ injection from a pn junction.

**Parameters:**
- c = 4.2 wt%, J = 15 mA/cm², t = 2.25 hours.

**Geometry:**
- Pore depth: 73 µm, spacing: 30 µm, wall: 3-4 µm.

---

Fig. 3.16 Macropore array formed in silicon by h^+ injection from a pn junction.

**Parameters:**
- c = 2.2 wt%, J = 7 mA/cm², t = 2 hours.

**Geometry:**
- Pore depth: 33 µm, spacing: 45 µm, wall: 2 µm.
3.3. Formation of 3D and free-standing structures

Not only macropore arrays but also three-dimensional structures can be formed by electrochemical etching [44]. The formation mechanism of 3D-structures by electrochemical etching is illustrated in Fig. 3.17. In fact, it is rather similar to macropore formation where the structures formed on the wafer surface prior to electrochemical etching serve to deflect the current lines. Similarly, the SCR passivates the structure. For a well designed mask and appropriate resistivity, no charge carriers will penetrate the structures and only the surrounding surface is etched. The goal is then to obtain polishing around the structure. This is observed in Fig. 3.18. Apparently, $J_2$ is at least equal to $J_{ps}$, and $J = 0$ in the structure. To compensate for the structure where $J=0$, $J_1$ is somewhat larger than $J_2$. This may be clearly seen in Fig. 3.18 where the area in proximity with the circular structure (area “1”) is smoother than that of area “2”, revealing a superior electropolishing reaction.

Fig. 3.17 Formation mechanism of 3D structures in n-type silicon using photogeneration.

Free-standing structures can also be formed by electrochemical etching. The idea is to first form a structure, which could be a macropore array for instance, and then, after a specific depth has been achieved, to increase the current to obtain electropolishing in order to release the structure from the bulk. This has been done on the sample presented in Fig. 3.19. It is of course possible to do the same using $h^+$ injection from a p-n junction, as demonstrated in Fig. 3.20.

Fig. 3.18 3D structure (a tube).
Parameters: $c = 2.2$ wt%, $L = 5.5$ cm, $J = 13.5$ mA/cm², $t = 2.33$ hours.

Fig. 3.19 Free-standing pore array. $c = 4.2$ wt%, $L = 4.5$ cm, $J$ was constant at the beginning and then increased.

Fig. 3.20 Free-standing letters: m and t. $c = 2.2$ wt%, $J = 7.5$ mA/cm² at the beginning and was increased to 8.5 mA/cm² to release the structure. $h^+$ injection from a p-n junction was used.
4 Detector processing and characterization

4.1. CCD-based detectors

4.1.1 Formation of macropore arrays

The first process step in the fabrication of the CCD-based detector is the formation of a macropore array in silicon. Two techniques were used: electrochemical etching (EE), which was presented in chapter 3, and deep reactive ion etching (DRIE, Fig. 4.1).

DRIE
Following a standard photolithography step in order to pattern the surface, the process consists of alternating between an etching cycle in a SF₆ plasma and a passivation cycle in a C₄F₈ plasma [45]. Each cycle lasts for about 10 seconds. The initial mask can be made of oxide or photoresist, whose etching selectivity is 120:1 to 200:1 and 50:1 to 100:1, respectively [46]. Silicon atoms are chemically etched away due to the interaction with the species of the SF₆ plasma. A polymer film is deposited on the wafer surface during the C₄F₈ plasma cycle and is used to protect the pore walls during the etching cycle. Macropores can be grown perpendicularly to the silicon surface independently on the type (p or n), the resistivity and the crystallographic orientation, which may, on the other hand, affect the etch rate. A disadvantage of DRIE is the rough pore walls obtained by DRIE, while EE gives smooth walls.

DRIE versus EE
DRIE and EE are two complementary etching techniques. The former allows etching of pores with large walls but not deep pores of small diameter (limited at 200-μm deep pores with a diameter around 10 μm). The later allows diameters ranging from less than 1 μm to more than 100 μm for very deep pores but the pore wall thickness is limited. Generally, DRIE enables to etch pores with a maximum aspect ratio of about 20, while EE enables aspect ratios up to 250.

Fig. 4.1 Example of a macropore array made by DRIE. (A) Top view, (B) Cross-sectional view.
In DRIE, in principle any pattern could be used to form pores whereas for EE a repetitive pattern must be used. Otherwise, pores will form randomly in between structures. In practice, however, the DRIE etching parameters depend on the used pattern, requiring optimization for the particular structure used.

The geometry of the macropore array has a strong influence on the detector performance:

- The pore spacing will determine the spatial resolution of the detector if the pixel pitch of the CCD is smaller. The largest pitch of the two (CCD and pore array) determines the detector spatial resolution. A pore spacing of 45 µm would lead to a spatial resolution of about 11 lp/mm.
- The pore depth is related to the detector efficiency since very deep pores are preferable for a large thickness of scintillator. A 250-µm thick CsI layer absorbs about 80% of incoming X-rays. However, too deep pores would lead to low wave-guiding efficiency.
- The pore wall thickness, which is related to the pore diameter, determines the active area. Thin pore walls are preferable for high active area. However, too thin walls would allow light transmission between the wave-guides.

4.1.2 Reflective layers on the pore walls

As indicated in Fig. 2.4(B), the performance of the detector relies on efficient guiding of the secondary photons towards the CCD. Thus, reflection at the pore walls would improve the detector efficiency. Two methods can be used in order to reflect the light emitted from the scintillator. A 2 µm-thick silicon dioxide layer (SiO$_2$) can be grown by wet oxidation at 1100°C for 9 hours. Longer oxidation times were experimented but no significant change on the detector efficiency was noticed. Figure 4.2 shows a 5 µm-thick SiO$_2$ layer at the bottom of a DRIE pore. Using an oxide layer, the reflection coefficient depends on the incidence angle of the photons and only a part of the photons will be reflected. Photons of incidence angle lower than the critical angle will be totally reflected. Less than 20% of the photons emitted by the scintillator would be reflected towards the CCD pixels using 250-µm deep pores with a diameter of 40 µm.
The other alternative is to use a metal layer. Atomic layer deposition (ALD), which is a kind of chemical vapor deposition (CVD), can be employed to deposit Ruthenium (Ru) or Platinum (Pt) \[47\]. A thin Al₂O₃ film is usually pre-deposited by ALD on the surface in order to improve adhesion of the metal layer. Typical thicknesses are in the range of 100 nm. Ru coated macropore arrays are shown in Fig. 4.3. This technique is promising and can provide conformal deposition on large areas. The metal was also deposited on a planar wafer and the reflectivity was measured to be about 70% at 550 nm, the emission wavelength of CsI (Tl). Note that other techniques, such as the arc-discharge method and evaporation, were experimented but were not successful.

4.1.3 Filling of pores with CsI(Tl) and CsI(Na)

The technique employed to fill the pores is described in appended paper A. A schematic of the sample holder is given in Fig. 3 of appended paper A. The idea is to cover the pore array with CsI powder, which is then melted into the pores. Thus, the choice of CsI was also motivated by its low melting point as compared to silicon, 621°C and 1410°C respectively. The sample was immersed in the CsI liquid for a few minutes (typically 5 min) to ensure a complete filling of the pores and then cooled down at around 10°C/min. The dependence of the detector efficiency as a function of cooling rate is reported in appended paper A and shows an optimal value at about 10°C/min. A spring maintained the sample in thermal contact with the sample holder to prevent it from floating over the melt. The setup was installed in a hermetic chamber and the process was made in nitrogen (N₂) ambient. Once the cooling phase was over, any residual CsI on top of the sample was removed mechanically. This polishing procedure requires special precautions because of the fragile structure of the matrix and because CsI dissolves in most liquids. Silicon oil or ethylene glycol may be used. SEM images of filled macropore arrays are presented in Figs. 4.4 and 4.5.

Fig. 4.4 SEM image of an oxidized matrix filled with CsI(Tl). The image on the right hand side illustrates some of the defects observed in the CsI guides.
As can be seen from these images, CsI is a very soft material, which does not make easy the evaluation of the filling quality. Indeed, parts of the CsI are missing and it is hard to find the origin. It could be a part that fell out due to cleaving or a part that has never been there due to a non-complete filling of the pores. However, photoluminescence and SEM images suggest that defects are present in the CsI waveguide due to gas bubbles [24, 25]. Some experiments were therefore performed under vacuum, but sublimation of CsI occurred before 600°C and the scintillator was deposited on the glass window of the chamber. All experiments were then done in nitrogen ambient in order to properly fill the pores and minimize oxidation of the setup. These defects (bubbles) in the CsI waveguides are detrimental for the detector efficiency since it lowers the guiding efficiency. As can be seen in Fig. 4.5, CsI is not in complete contact with the metal. This gap between CsI and the wall, especially at the pore bottom, is also observed for oxidised walls. The diminution of the CsI volume during cooling, due to the different thermal expansion coefficients, may explain this gap. From these images, the metal layer does not seem to be affected by the treatment at 621°C. No formation of silicide seems to occur. However, the metal presents a certain roughness, which may lower the reflectivity of the walls.

4.1.4 X-ray characterization and imaging

The macropore arrays presented above were then mounted on top of a CCD in order to realize the final detector and measure its performance. No particular alignment was made between the CCD pixels and the CsI columns. An optical fiber plate was placed between the CCD and the matrix. This plate protects the CCD from direct X-ray exposure. Results of an oxidized pore matrix filled with CsI(Tl) is presented in appended paper A. The matrix was an array of 238 µm deep pores spaced at 45 µm and having 6.2 µm thick walls (2 µm of oxide on each side). The spatial resolution was measured using a metallic pattern as object placed on top of the detector. The X-ray source was a standard dental source operating at 60 kV. A spatial resolution of about 9 lp/mm was obtained while the calculated one, according to the pore spacing, was 11 lp/mm. A SNR of 50 was obtained at 27 mR, which is in the range of what dentists usually use with photographic techniques. Simulations of the detector are presented in Ref. 48 and are in good agreement with experimental results. The efficiency of the matrix is mainly limited by the poor guiding efficiency of photons emitted from the
scintillator, which is related to the matrix geometry, the use of oxide as a reflective layer, and the defects contained in the CsI guides. Figure 4.6 shows an image of a pattern, using also an oxidized matrix filled with CsI(Tl). These images clearly indicate that the scintillating guides screen improves the image quality and that a spatial resolution of about 10 lp/mm can be reached.

![Image given from the CCD covered with the matrix.](image1)
![Image given from the CCD only.](image2)

Fig. 4.6 X-ray image of a pattern used to determine the spatial resolution of the detector. The matrix covers only the center part of the whole CCD area. The periphery is the image given by the CCD only.

Similar experiments were performed with metallized matrices, as shown in Fig. 4.5. The performance of the detectors, especially the SNR, was compared with that of one of the best oxidized macropore matrices. All metallized matrices showed lower performance with a SNR more than two times lower. However, no dramatic differences can be seen in Figs. 4.4 and 4.5 between the CsI(Tl) filling of an oxidised and a metallised matrix. Silicide does not seem to form during the filling process, and the pores seem to be completely filled. The main problem that can be seen from Fig. 4.5 is that CsI is not in complete contact with the metal. This gap may explain the low efficiency of the metallized matrices but not the difference in comparison with the oxidized matrix. However, the CsI filling process is still not perfect and results in presence of defects in the CsI guides. It is important to note that large differences in the performance of detectors fabricated in a similar manner have already been measured. Part of this problem could be that Tl is segregated into the liquid during the melting/crystallization process in the pores. This would result in an inhomogeneous Tl concentration with a following reduction in efficiency. Thus, it may be necessary to repeat this comparative study between metallized and oxidized matrices with a more reliable filling process.

CsI(Tl) and CsI(Na) have been used to fill the pores. Higher efficiency have been obtained from matrices filled with CsI(Tl), which may be explained by the emission wavelength of the scintillator. Indeed, CsI(Tl) emits light at 550 nm, which is very suitable to a CCD, while CsI(Na) emits at 420 nm where the CCD is less sensitive.
4.2. CsI-photodiode structure

Similar macropore arrays as for the CCD-based detector concept were used here. The challenging step of the detector fabrication is, this time, the formation of p-n junctions in the pore walls, cf. Fig. 2.7. Two doping techniques were used and results are reported in appended paper B.

4.2.1 p-n junction formation by boron diffusion

Boron diffusion from a solid source has been used to form p-n junctions in the silicon pore walls. The initial macropore arrays were made in n-type silicon by EE.

A first diffusion was performed at 1150°C for 105 min (diff1) in a nitrogen atmosphere. A thin oxide layer was formed during the temperature ramp down in an oxygen atmosphere to prevent out-diffusion of boron. This oxide was then removed in hydrofluoric acid. Figure 4.7 shows a SEM image of the sample after diffusion. A 3 µm thick layer brighter than the bulk can be seen at the pore bottom, and is believed to be the diffused boron layer. Scanning spreading resistance microscopy (SSRM) was used in order to confirm this observation. SSRM is a kind of atomic force microscopy (AFM). AFM is a technique where the topography of a sample is obtained by scanning the surface with a probe. In SSRM, the spreading resistance is measured during scanning and the doping distribution in the structure can be recalculated and imaged at the same time. Similarly, scanning capacitance microscopy (SCM) measures the capacitance variation between the probe and the sample, which enables also to image the doping distribution. The doping distribution measured by SSRM is shown in Fig. 4.8, suggesting the presence of a 3 µm thick highly conductive layer at the pore bottom, in agreement with the SEM image.

As can be seen from Fig. 4.7, the pore wall is apparently completely doped with boron; thus, no p-n junction has really been formed in the wall. SIMS was used to measure the doping profile through the pore wall thickness. The cross-section of the sample was polished and then mounted on the edge to perform the measurements. The profiles, taken at different positions along the pore depth, are shown in Fig. 4.9(B). It shows that the doping levels are in the same order of magnitude along the pore depth, at about $5 \times 10^{19} \text{ cm}^{-3}$. However, the same diffusion was performed in a planar sample and a 6 µm thick layer with a maximum boron doping of $2 \times 10^{20} \text{ cm}^{-3}$ was measured, as seen from profile a in Fig. 4.9(A). This higher doping
level, together with the larger thickness, indicates that the transport of boron down to the pore bottom limits the doping in macropores (at this temperature).

Another diffusion was performed at 1050°C for 70 min (diff2) in a nitrogen atmosphere. The SIMS profile measured in a planar sample showed a boron layer stretching up to 2 µm with a maximum boron doping of $2 \times 10^{19}$ cm$^{-3}$ (profile b, Fig. 4.9(A)). The SIMS profiles taken along the pore depth are shown in Fig. 4.9(C). The p$^+$ layers located on each side of the pore walls are clearly revealed in profile c. This time, the doping levels measured along the pore depth are in the same range as that measured in the planar sample, suggesting that the diffusion is not mass transport limited but maybe reaction limited, at this lower temperature.

4.2.2 p-n junction formation by LPCVD

LPCVD of boron doped poly-silicon was performed at 600°C under a pressure of 150 mTorr in the presence of SiH$_4$ and B$_2$H$_6$ for 90 min. The deposition was also done on a planar sample, whose SIMS profile is shown in Fig. 4.9(A), profile c. The layer is about 400 nm thick with a boron concentration of $5 \times 10^{19}$ cm$^{-3}$. The boron doped poly-silicon layers deposited on a DRIE-etched macropore array are shown in Fig. 4.10. The deposition is found to be conformal with a layer as thick at the top of the pores as at the bottom. The presence of a p-n junction at the pore bottom was also suggested by SCM analysis, as seen in Fig. 4.11.
4.2.3 Comments

Pores having p-n junctions in their walls can also be filled with CsI(Tl), as shown in appended paper B. However, other scintillators, with a scintillation wavelength close to 850 nm, may be preferable to match the photodiode sensitivity, as seen in Fig. 2.6. The other process steps are then to separate the p-n junctions of each pixel, one from another. A possibility would be to remove a few microns at the top of the array using a short reactive ion etching cycle or to protect the top of the walls prior to doping. However, there will still be the difficult task of making contacts to the p+ layers. As explained in section 2.2, this detector concept allows to detect the photons emitted from the scintillator at a relatively short distance from their generation point, giving supposedly high charge collection efficiency. Considering an optimal pore wall thickness of 4.1 µm, which is a compromise between optimization of the detector active area and the number of photons absorbed in the walls, an overall efficiency of 60% could be reached with this concept. However, simulations presented in Ref. 48 show hat the noise in the detector will be very high too, leading to relatively poor SNR.
4.3. Semiconductor-based detector – Thindrill results

As explained in section 2.3, the semiconductor-based detector concept requires the formation of macropores having thick walls (indeed functioning as the absorbing medium), which differs from the two other concepts where thin walls were needed. The formation mechanism using EE is the same as that presented in Fig. 3.8. For these narrow diameter pores, DRIE is less appropriate for two reasons: lower obtainable aspect ratios and for damaging the pore surface, later used for electrical contacts. The effect of the current density, illumination intensity and applied voltage is illustrated here. The pattern used gives a hexagonal repartition of the pores on the sample surface with a pitch of either 30 or 50 µm. A 20 W halogen lamp was used for photogeneration, except for the sample in Fig. 4.12. The illumination intensity was computer controlled and the voltages mentioned refer to the bias between the reference electrode and the sample back side. Figure 4.12 shows an example where the light apparently created EHPs in the pore wall. Thus, silicon dissolution occurred in the pore walls, leading to porous silicon. After some adjustments, particularly of the light source, proper macropore arrays could be formed in silicon, as seen in Fig. 4.13.

Fig. 4.12 Unsuccessful etching of pores leading to porous silicon in the pore walls.
**Parameters**: 300 W halogen lamp at L = 5 cm, c = 4.2 wt%, 1 V, J = 1.4 mA/cm², t = 2.15 hours.

Fig. 4.13 Successful etching of macropore arrays.
(A) **Parameters**: 20 W halogen lamp, c = 5.45 wt%, 0.8 V, J = 2.2 mA/cm², t = 8 hours.
**Geometry**: Depth: 270 µm, spacing: 30 µm, diameter: 12-14 µm.
(B) **Parameters**: 20 W halogen lamp, c = 5.45 wt%, 1 V, J = 1.35 mA/cm², t = 11.6 hours.
**Geometry**: Depth: 435 µm, spacing: 50 µm, diameter: 14 µm.
4.3.1 Effect of the current density

Figures 4.14 and 4.15 show SEM images of samples, whose etching conditions only differed from the etch time and the current density. As explained in section 3.2.1, the pore diameter is dependent on the current density and higher current density leads to larger pores. However, as can be seen from these images, pores etched at a lower current density are larger. This indicates that etching does not only occur at the pore tip but also in the pore walls. Nevertheless, this dissolution of the walls is very slow since the pores became 200 µm deeper and the pore diameter 3 to 4 µm larger during the same period of time. Diffusion of carriers in the walls may explain dissolution of the silicon pore walls. Another conclusion is that the etch rate is not linearly dependent on time. Indeed, according to the result obtained in Fig. 4.14, 9 hours of etching would lead to 630 µm deep pores, which is not observed in Fig. 4.15.

A study of the etch rate as a function of time (or pore depth) has been done by modulating the current density with a sinusoidal function. As a result, the pore diameter was also modulated by a sinusoidal function (with diameter scaling as $J^{1/2}$), as can be seen in Fig. 4.16. Clearly, the pore growth rate is not constant along the pore depth. The pore growth rate was rather fast at the beginning, about 1.1 µm/min, and then reached saturation at about 0.5 µm/min. The pore growth rate as a function of pore depth is shown in Fig. 4.17. The slow etch rate at the pore bottom may be explained by a slow HF molecules mass transport, only subject to diffusion, as compared with the F⁻ ions transport, subject to the diffusion and migration. This disturbs the balance between the HF molecule and the F⁻ ion concentrations at the pore bottom. Thus, the tetravalent reaction is favored at the pore bottom while the divalent reaction is favored at the top, which may explain the decrease of the etch rate by a factor of roughly 2.

At about half the pore depth, the pore diameter was $\bar{D}_1 = 13.5$ µm for 1.35 mA/cm² and $\bar{D}_2 = 16.8$ µm for 1.95 mA/cm², which confirms the dependence of the pore diameter on the current density. The current at the pore tips were $J_{tip1} = 29.2$ nA and $J_{tip2} = 42.2$ nA. There is a relatively good agreement between the ratios $(J_{tip1} / J_{tip2}) = 0.69$ and $(\bar{D}_1 / \bar{D}_2)^2 = 0.645$.

Finally, Fig. 4.18 illustrates the effect of non uniform pattern. If one pore is missing in a row, $h^+$ will be consumed in the neighboring pores, deforming their pore shape.
Fig. 4.16 Thin macropore array. (A) Cross-sectional view, (B) Zoom in at the bottom of a pore.

**Parameters:** $c = 5.45$ wt%, $0.8$ V, $t = 9.33$ hours, sinusoidal variation of $J$: $1.35 < J < 1.95$ mA/cm$^2$, period: 45 min.

Fig. 4.17 Local pore growth rate as a function of pore depth for the sample presented in Fig. 4.16. The etch rate was calculated as follows: (Depth etched during 45 min) / 45 min

Fig. 4.18 SEM image showing the importance of uniform pore distribution at the surface. The effect of a missing pore is pointed by arrows.
4.3.2 Effect of the applied voltage

The effect of the voltage applied on the sample is shown in Fig. 4.19. The evolution of the pore shape is in agreement with observations made in Ref. 40. A star-like shape of the pores is obtained at high voltages. Clearly, voltages in the range of 1 V should be used to grow proper macropores. This experiment shows also that etching occurs at the pore corners. The influence of the bias on the pore shape has not really been explained yet. Although these experiments were performed in highly resistive silicon samples, some believes that electrical breakdown is responsible for this phenomenon.

Fig. 4.19 Macropore arrays formed at different anodic bias.
Common parameters: c = 5.45 wt%, J = 1.4 mA/cm², t = 1.66 hours.
Summary, conclusions and outlook

The main challenges for new X-ray imaging detectors are high spatial resolution and high signal-to-noise ratio at low X-ray doses, crucial parameters with regard to the patient health. Thus, different detector designs are proposed. In this thesis, the technological development of three different types of X-ray imaging detectors was studied. All the proposed detector concepts were based on macropore arrays formed in silicon. Both DRIE and EE were employed. However, EE was deeper studied and developed. Particularly, EE of n-type silicon using hole injection from a p-n junction was found to be a successful alternative to photogeneration. Further study is, however, still required for a better understanding of the charge transfer occurring at the electrolyte/silicon interface during the chemical reaction. In addition, subsequent processing of these macropore arrays was studied. The recent advances as well as the further tasks to be done for each detector concept are presented below.

The first detector type is based on a CCD, whose pixels match wave-guides of a scintillating screen formed by filling a macropore array with CsI(Tl). Macropore arrays with a pitch of 45 $\mu$m, pore depths up to 400 $\mu$m and pore wall thickness in the range of 4 $\mu$m were fabricated by EE. Such geometry leads to active areas higher than 80% and a scintillator thickness enabling to absorb more than 80% of incoming X-rays of a standard dental source. Both oxide and metal were used to reflect the photons emitted from the scintillator on the pore walls. The pores were filled by melting the scintillator. Detectors were fully fabricated and presented good spatial resolution (10 lp/mm) but SNR values and X-ray doses were only in the range of already available devices. Nevertheless, it should be noted that the technique developed to fill the pores with CsI(Tl) still suffers from a low reproducibility and presence of defects. The use of metal as a reflective layer could also, in principle, improve the wave-guiding property of the scintillating wave-guide screen.

The second detector type required formation of macropore arrays in n-type silicon, which can be achieved by EE or DRIE. In this concept, the visible light generated in the scintillator is not detected by a CCD but by photodiodes formed in the macropore walls. Both boron diffusion from a solid source and low-pressure chemical vapor deposition of boron doped poly-silicon were shown to be suitable techniques to form these photodiodes. Further tasks are to measure the current-voltage (IV) characteristics of such diodes and to make contacts to the p$^+$ layers. Simulations of such a detector predicted high charge collection efficiency, but unfortunately, a signal-to-noise ratio limited by the absorption of X-rays in the silicon photodiodes.

The third detector concept uses bulk silicon as a detecting material. Arrays of deep and narrow holes with a pitch of about 50 $\mu$m had to be formed. Results presented in this thesis show 435-$\mu$m deep pores with a diameter of 14 $\mu$m, leading to an active area around 90% and an aspect ratio up to 30. Next process steps are to metallise the pores and to bond the array to a readout circuit. Such demonstrators are currently in process. The difficulty with this...
detector principle is the low absorption coefficient of Si for X-rays. Thus, other materials of higher X-ray stopping power than silicon, such as GaAs, could be used.

In conclusion, deep macropore (up to 400 µm) arrays with a pitch of 50 µm and pore diameters ranging from 10 to 40 µm were formed by EE. In some cases, DRIE could be used too; however, as demonstrated in this work the achievable aspect ratio using EE far outperforms that of DRIE. In addition, this study shows the possibility to process the pore walls: (i) formation of reflective walls by oxidation or metallisation and (ii) formation of photodiodes by doping the walls (diffusion and LPCVD). Further, the pores can be filled by a scintillator. However, some more technological development is still required to fully fabricate some of the detectors, as for instance the formation of electrical contacts in the CsI-photodiode structure. It would be very interesting and helpful to entirely fabricate and characterize these detectors in order to optimize them. Finally, nanopore arrays, instead of macropore arrays, could be formed to obtain detectors of very high spatial resolution. For this, EE would be a suitable technique.
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