CHAPTER 1

INTRODUCTION

Increasing the pixel density of camera chips is an ongoing trend in the camera industry. Since almost every smart phone, tablet, television or even glasses has a camera, the demand for higher pixel density and smaller chips which have higher resolution is ever increasing. So far, shrinking the usual structures and improving readout algorithms has been sufficient to meet the demand. However, the limits in shrinking normal CMOS photodiode structures have almost been reached. Therefore, a new concept for photodiodes is needed. Instead of using four pixels for one information point, one blue and red pixel and two green - the so called Bayer filter [2] - only one pixel could be used by stacking the diodes on top of each other. Furthermore, it would reduce problems of today's Color Filter Arrays (CFA), as they suffer from color aliasing effects [3, 4]. This would result in one pixel which could detect red, green and blue light and also reduce the space needed. To achieve this goal, the wavelength dependency of silicon can be taken advantage of. Light of different wavelengths is absorbed at different depths inside the silicon crystal. Red light penetrates the silicon much deeper than blue light. By stacking p-i-n diodes on top of each other, with different intrinsic regions designed to absorb light with a specific wavelength this would be possible. The photocurrent in the different regions, generated by the recombining light, can be interpreted as color information. There are several concepts which use the wavelength dependency of silicon, a lateral structure using a transverse field detector or a vertical structure. Several structures have been explored to fabricate sensors: selective epitaxy pnpnnp, transparent conductive oxide (TCO)-nipiin, TCO-pin-TCO-nip-TCO-pin, nppn, pinip and ppnp [5–10]. These are able to detect different colors by using the wavelength dependency of silicon. Some of the sensors have other applications besides photography, for example, to sense whether the device is used outside or indoors, which can be detected by analyzing the spectral distribution of the light source. Furthermore, different material combinations as well as different illumination conditions, biasing and manufacturing methods were also explored. The motivation of this work was to explore the possibility of a MESA[1] structured stacked photodiode which could be used as a color detector.

In this work a new approach of vertically stacked photodiodes is presented. The device was developed and fabricated in the clean room of the Institute of Physics at the Universität der Bundeswehr München. It utilizes the wavelength dependent absorption of monocrystalline silicon for the differentiation of colors. Monocrystalline silicon has the advantage that light can allready penetrate the structure deeper before the absorption process takes place. The approach in this work is based on a vertical MESA structure which opens up many different possibilities of structuring, connecting and designing of devices which would not be possible in the normal lateral approach, for example, vertical tunnel field effect transistors.
At the time of writing, stacked photodiodes with a MESA structure are still in an early stage of development. Since vertically structured MESA devices for photodiodes are new, many aspects are still unknown. It should be kept in mind that the vertical approach has great potential to replace commonly used CFA based color image arrays.

Chapter 2 recapitulates important details about the basics of chemical vapor deposition (CVD) which is used for the epitaxial structure of the device. Furthermore, the optical behavior and properties of a silicon based p-i-n photodiode are explained.

Chapter 3 explains the need for good crystal quality in semiconductor devices and the importance of reliable information about the layer thickness.

Chapter 4 contains the main body of this work. It explains in detail the manufacturing process and the substantial improvements to the contacting, passivation and etching process. Furthermore, the need for good crystal quality, layer thickness and highly doped δ-layers is explained.

Chapter 5 shows the electrical characterization of the experimental results. Two different approaches of measuring are explained for the top and bottom diode. In addition, the data is compared to theoretical expectations as well as simulated data, and explanations are given accordingly.

Finally, **Chapter 6** concludes that almost all theoretical predictions could be verified experimentally.

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[1] mesa is Spanish for table, and means an elevated area of land with a flat top and sides that are usually steep cliffs [11, p. 166]

CHAPTER 2

THEORY

The main element of every functional semiconductor device is its p-n junction. They can be created using implantation, diffusion or deposition. This chapter will explain the basics of the widely used CVD. Furthermore, the basics of p-n junctions as well as p-i-n junctions are explained with a special interest in the optical properties of p-i-n junctions.

2.1 Epitaxy

The therm epitaxy originates from the Greek words epi $\epsilon\pi\iota$ meaning “upon” and taxis $\tau\alpha\xi\iota\varsigma$ meaning “in ordered manner”. Which can be translated as “arranging atoms upon a substrate”. Meaning that a crystalline layer can be grown on a crystalline substrate with the same crystallographic orientation as the substrate. There are different forms of epitaxy, the homoepitaxy where the deposited material is the same as the substrate, and the heteroepitaxy in which a crystalline film grows on a crystalline substrate or film of a different material, for example, $AlGaAs$. [12, p. 45]

2.1.1 Silicon epitaxy by Chemical Vapor Deposition

CVD is commonly used to deposit solid films with gaseous precursors on a substrate. CVD is based on a chemical reaction where the reactive gaseous precursors of the depositing material, for example, Si_2H_6 for silicon forms a layer on the surface. This layer is created through the separation of the precursors on the surface in one solid part and one gaseous part. If more than one precursor is present in the current gas flow, interaction between gases is possible.

For CVD, the current flow inside the CVD reactor is an important factor. The material transport on the surface of the wafer is dependent on the current flow. The flow region can be either

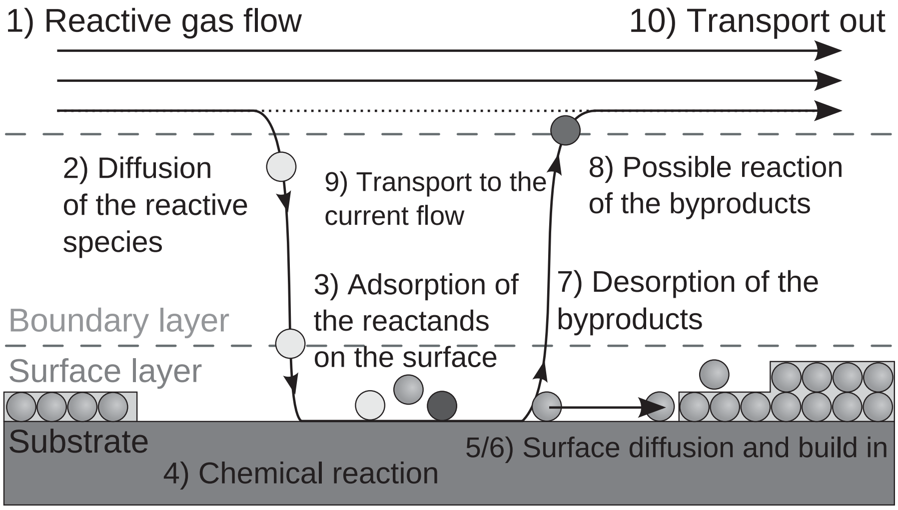


Figure 2.1: Schematic sequence during CVD

molecular flow or viscous flow. It is dependent on the type of CVD, either at atmospheric pressure or at lower pressures. It can be characterized through the dimensionless Knudsen number, which is defined in equation 2.1. [13, p. 59-62]

$$Kn = \frac{\lambda_{MFP}}{l_{char}} \tag{2.1}$$

Here λ_{MFP} is the mean free path and l_{char} the characteristic length of the flowed through diameter. Table 2.1 summarizes the different regions with their respective Knudsen number. Between molecular and viscous flow, there is a transient zone called Knudsen-flow. [13, p. 59-62]

Table 2.1: Overview of possible flow regions

Knudsen	**Flow type**	**CVD-method**
$Kn \geq 1$	molecular flow	GS-MBE
$0.01 < Kn < 1$	Knudsen-flow	UHV-CVD, VLP-CVD
$Kn \leq 0.01$	viscous flow	LP-CVD, RP-CVD, AP-CVD

The reactor used in this work operates in the viscous flow region. Figure 2.1 shows the principle deposition process, with the steps shown below. Viscous flow is described through the molecular interaction of the gas molecules [13, p. 59-62][12]. The molecular and Knudsen flow regions are not used in this work and will therefore not be discussed.

1. Reactive gas flow over the substrate
2. Diffusion of the reactive species through the boundary layer
3. Adsorption of the reactants on the surface
4. Chemical reaction on the surface

5. Surface diffusion
6. Build in of the atom into the crystal lattice
7. Desorption of byproducts of the reaction or unused reactants
8. Possible reaction/interaction of the byproducts
9. Transport of the products through the boundary layer
10. Transport out of the reactor with the main gas flow

For CVD deposition, the transport of the reactive gas species from the main gas current to the substrate is essential for a chemical reaction. The concentration gradient between the main flow C_{bulk} and the surface concentration C_{surf} through the boundary layer δ is after Fick's law of diffusion the main force for a balanced diffusion density j_{diff}. The particle density is given through the respective partial pressures p_b or p_s (equation 2.3).

$$j_{diff} = D \cdot \frac{C_{bulk} - C_{surf}}{\delta} = \frac{D}{\delta} \cdot (C_{bulk} - C_{surf}) \tag{2.2}$$

$$C_{bulk} = \frac{p_b}{K_B T}; C_{surf} = \frac{p_s}{K_B T} \tag{2.3}$$

D is the diffusion constant which is dependent on the respective molecule class as well as the pressure p and the gas temperature T (equation 2.4). [14, 15]

$$D = D_0 \left(\frac{T}{T_0}\right)^{\beta} \frac{p_0}{p} \tag{2.4}$$

D_0 is typically in the range of $0.1\,\mathrm{cm^2\,s^{-1}}$ to $1.2\,\mathrm{cm^2\,s^{-1}}$ and β is usually between 1.75 and 2 [15]. $p_0 = 1013\,\mathrm{mbar}$ and $T_0 = 273\,\mathrm{K}$ are the typical values under normal conditions. [13]

2.1.2 Growth process

To describe how the different growth regimes of CVD work, a simplified model is assumed. When a precursor comes into contact with the surface it will react completely and the byproducts will desorb completely without reaction steps between, as described in 2.1.4. To simplify the reaction further, silane (SiH_4) is used to explain the following processes, because it only has hydrogen as a byproduct. Through this measure, the reaction is reduced to steps 1 to 7, as described in section 2.1.1. For CVD deposition, the transport of the reactive gas species from the main flow to the substrate is essential for a chemical reaction. The adsorption and desorption process on the surface defines the equilibrium concentration C_{eq}. After the concentration exceeds a certain point effective absorption in the range of a characteristic absorption length l_{ad} is possible, through a supersaturation ($C_{surf} - C_{eq}$). The surface reaction, with the reaction coefficient k_s, will dominate for a certain temperature range. Figure 2.2 a) illustrates the different regions of the process, which will be explained in the following section. Figure 2.2 shows measured growth rates and calculated activation energies. [13]

$$k_s = k_0 \exp - \frac{E_a}{k_B T} \tag{2.5}$$

T is the substrate temperature in K, E_a the typical activation energy in eV and k_B the Boltzmann constant. k_0 is a pre-exponential factor with the unit s^{-1}. For the two-dimensional deposition (equation 2.6), described through the particle current j_{chem} of chemisorbed molecules, with k_d as mass transfer coefficient. [14]

$$j_{chem} = k_s \cdot l_{ad} \cdot (C_{surf} - C_{eq}) = k_d \cdot (C_{surf} - C_{eq}) \tag{2.6}$$

For equilibrium conditions $j_{chem} = j_{diff}$ it is possible to calculate the surface concentration C_{surf} from equations 2.2, and 2.6. Sh is the so called Sherwood number, which can also be called Nusselt number. It is a dimensionless number used in mass-transfer operations. [13]

$$C_{surf} = \frac{C_{bulk} + Sh \cdot C_{eq}}{1 + Sh} \tag{2.7}$$

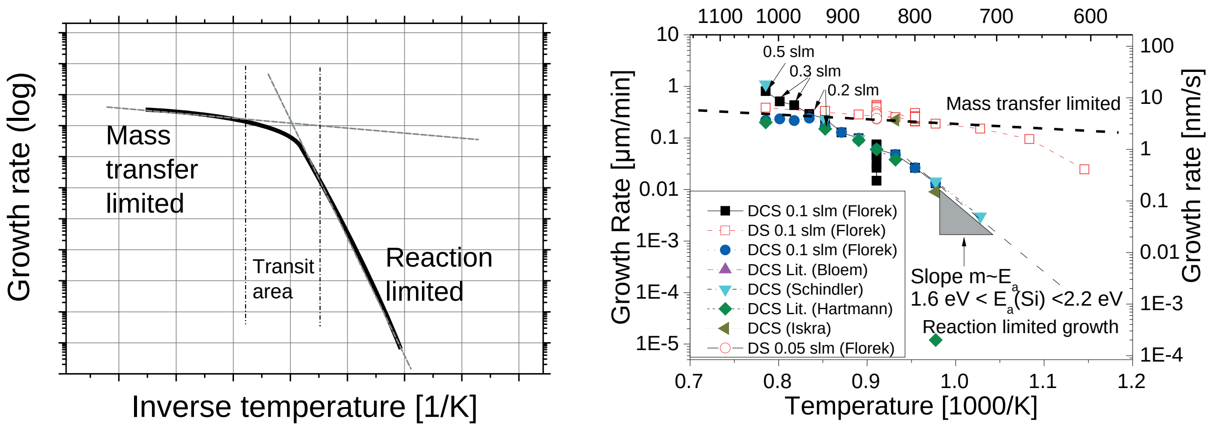
$$Sh = \frac{k_d}{D/\delta} = \frac{k_d \cdot \delta}{D} \tag{2.8}$$

Reaction limited growth region $Sh \ll 1$ where k_d is limiting the process
In this case the reactive species diffuse through the boundary layer between surface and main gas current. The partial pressure of the reactive species can be assumed to be constant in the whole reactor. The growth rate $r_{reaction}$ can be plotted against the inverse temperature, the so called Arrhenius-plot (figure 2.2), which shows a typical exponential dependence in the reaction limited growth region. [13]

$$r_{reaction} = r_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{2.9}$$

E_a is the typical activation energy for the reaction. r_0 is a pre-exponential factor with the unit s^{-1}. Because the diffusion factor does not limit the reaction, the reaction limited growth is often referred to as reaction limited regime. Furthermore, the growth rate is very sensitive to temperature changes and can be described by the Arrhenius law. [13]

Transit area $Sh \approx 1$
This transit area is approximately 100 °C wide and both reaction coefficients must be taken into account. This region can be disregarded in this work because the deposition processes were outside this region. [15]



(a) Theoretical growth regimes with CVD

(b) Measured growth rates with the activation energy

Figure 2.2: Theoretical and measured growth rates

Rate of arrival or mass transfer limited region $Sh \gg 1$ where $\frac{D}{\delta}$ is the limiting process Here, the reaction on the surface is much faster than the transport to the surface, hence it is called rate of arrival. For $Sh \gg 1$ the fast chemical reaction on the surface dominates, hence equation 2.7 yields $C_{surf} \approx C_{eq}$. Therefore, the slow diffusion process limits the growth process, since the process is always dominated by the slowest process in the chain. [13]

At low temperatures the growth rate is reaction limited. The slope of the reaction limited growth is the activation energy E_a. The activation energy can be calculated from the slope using equation 2.9 if the diagram is an Arrhenius plot.

$$slope = -\frac{E_a}{k_B} \tag{2.10}$$

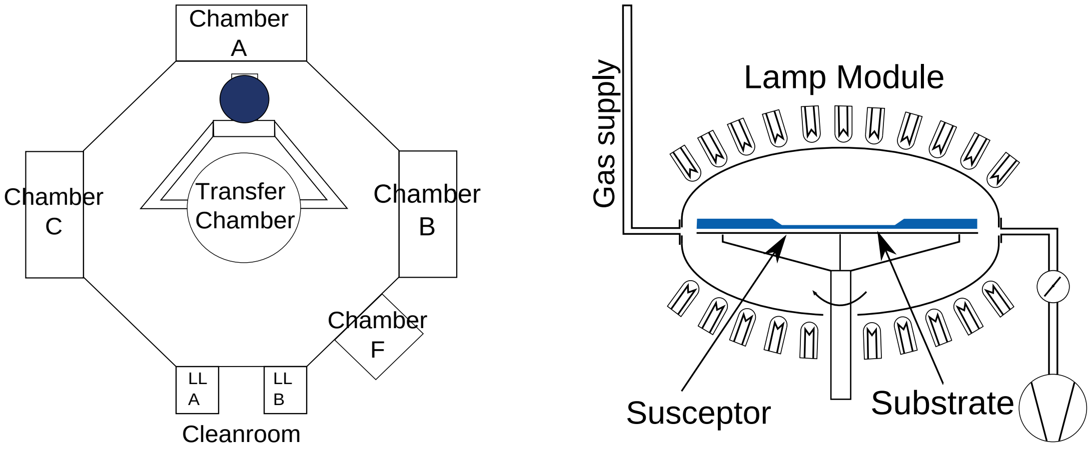
When the temperature rises, the slope decreases. When the slope reaches approximately $\frac{1}{2}$, it reaches the mass transfer limited growth regime. The mass transfer limited growth regime can also be influenced through the process pressure.

The modern semiconductor industry uses low pressures and low temperatures inside the mass transfer limited growth regime to obtain good conformity and sharp doping profiles at reasonable growth rates. In this work, the growth rate was monitored by weighing the wafers before and after growth.

2.1.3 Epitaxy Tool

To deposit the different silicon layers for this work, an Applied Materials Centura HT epitaxy chamber was used. This system is a multi-chamber cluster tool which consists of three different process chambers and four chambers for wafer handling (figure 2.3 a)). The process chambers are next to the epitaxy chamber, a metal-organic chemical vapor deposition (MOCVD) and a rapid thermal processing (RTP) chamber. Theses chambers are connected to the central transfer chamber which has a robot arm to move the wafers from the two connected load locks to the process chambers. After the processes are completed, the handler returns the wafer to a cooling chamber and then back to the load lock. The RTP and MOCVD chambers were not used in this work and will not be discussed any further.

The tool was designed to handle 200 mm wafers, 25 wafers in every load lock. To process smaller substrate sizes “adapter” wafers were used. These “adapter” wafers are 200 mm wafers with indentations etched into them which are the size of the smaller substrate.



(a) Cluster tool

(b) Process chamber A

Figure 2.3: Simplified schematic layout of the AMAT Centura platform and of the epitaxy chamber

The epitaxy chamber has four main components: the chamber dome, two lamp modules and the susceptor (figure 2.3 b)). The chamber dome is produced entirely from quartz glass to ensure optimum light transmission. Above the dome and below the process chamber, there is a bank of lamps each consisting of twenty 2000 W lamps. The radiation from the lamps is directed on a susceptor made of graphite coated silicon carbide. The wafers are loaded onto the susceptor for processing and can be heated at rates ranging from $5\,^{\circ}\mathrm{C\,s^{-1}}$ to $30\,^{\circ}\mathrm{C\,s^{-1}}$. The temperature is measured by two pyrometers, one for the top of the wafer and one for the back of the susceptor. Through this, only the wafer is heated and the walls of the chamber remain colder thus minimizing the coating of the walls. The process pressure of the chamber can be varied through a butterfly valve between 5 torr to 760 torr.

The gas supply of the chamber consists of different gases: purge, clean and process. The purge gas is nitrogen (N_2). For cleaning there is hydrogen chloride (HCl) which can also be used for etching. The process gases are hydrogen (H_2), dichlorosilane (SiH_2Cl_2), disilane (Si_2H_6) which can produce doped layers if a dopant gas is introduced into the flow. The dopant gases are phosphine (PH_3) for n-doped and diboran (B_2H_6) for p-doped layers. There is also the possibility for silicon germanium (SiGe) layers with germane (GeH_4) as process gas. Silicon germanium layers were only used to induce stress into the lattice to generate defects inside the layer. The SiGe layers were not characterized or used in a functional stack and will not be further discussed. The concentrations of the gases can be found in Appendix A.1.

2.1.4 Precursor gases

Precursor gases are fundamental for CVD, only through them are different kinds of layers possible. The tool used in this work operates in the viscous flow region. In this flow region, the gas can react with itself, since intermolecular collisions dominate the process [16]. The precursor gas reacts to different stages of reactive molecules within the gas before it diffuses to the substrate. The probability of these reactions increases with temperature and pressure. It is possible to suppress or enhance the reaction with carrier gases like hydrogen. [17]

For the successful deposition of silicon, process temperatures between 600 °C and 1200 °C are needed. Precursor gases which have more chlorine in their molecular structure need higher temperatures from the beginning. The benefit of chlorine based precursor gases is, that there is a sub reaction which etches parallel to the deposition process. This technique makes it possible to achieve better crystal quality at lower temperatures. Furthermore, with chlorine based precursors, selective epitaxy is possible. [17]

Disilane

Disilane (DS) is more reactive in comparison to commonly used silane (SiH_4). The weak Si-Si bond between the two SiH_3 is responsible for the higher reactivity. These dissociate through a reaction chain to monohydrides and in the last step to silicon on the surface. The last dissociation step of hydrogen is the limiting factor of the growth rate. The following reaction shows a possible reaction chain of DS. It is also possible to deposit different types of silicon, for example, polysilicon, α-silicon, which makes DS a versatile gas for CVD [18]. Where $Si(s)$ refers to a surface dangling bond site, $Si(b)$ a subsurface (bulk) atom, and $Si_2H_6(g)$ to an gaseous state.

$$Si_2H_6(g) + 2Si(s) \rightleftharpoons 2SiH_3(s) + 2Si(b) \tag{2.11}$$

$$SiH_3(s) + Si(s) \rightleftharpoons SiH_2(s) + SiH(s) \tag{2.12}$$

$$SiH_2(s) + Si(s) \rightleftharpoons 2SiH(s) \tag{2.13}$$

$$2SiH(s) \rightleftharpoons 2Si(s) + H_2(g) \tag{2.14}$$

Dichlorosilane

The interaction of dichlorosilane (DCS) with the silicon surface is complex in comparison to chlorine free gases, for example, DS. A model from *Coon et al.* [19] describes the reaction chain of the DCS-molecule on the surface. Similar to the DS process, the silicon is built into the surface and the hydrogen can desorb from the surface. The chloride part desorbs in the form of hydrogen chloride (HCl) or silicondichloride ($SiCl_2$). The formation of the silicondichloride is the part of the reaction which is responsible for etching. The deposition and etch processes are always parallel throughout the growth process. This makes it possible to achieve better crystal quality because part of every layer is always etched away. If the DCS part would be increased at one point, the etching process would dominate. A possible reaction chain is given below.

$$SiH_2Cl_2(g) \rightleftharpoons SiH_2Cl_2(s) \tag{2.15}$$

$$SiH_2Cl_2(s) \rightleftharpoons Si(s) + 2H(s) + 2Cl(s) \tag{2.16}$$

$$2H(s) \rightleftharpoons H_2(g) \tag{2.17}$$

$$H(s) + Cl(s) + \rightleftharpoons HCl(g) \tag{2.18}$$

$$2Cl(s) + Si(s) \rightleftharpoons SiCl_2(g) \tag{2.19}$$

2.1.5 Doping Gases

To fabricate working semiconductor microchips p-n junctions are needed. These junctions can be either diffused, implanted or deposited with doping gases. The doping gases are mixed into the precursor gas flow during the layer deposition, the so called (*in situ doping*). Through high temperatures the doping gases split and are built into the crystal lattice.

Diborane (B_2H_6)

The pyrolysis of diborane is similar to that of a precursor gas. Diborane is used to deposit p-doped layers. The reaction equation is given below [20]. Boron is known to have a better solubility in silicon than phosphorus. Also, unlike phosphine there are no segregation effects with diborane during growth, which makes it easier to handle.

$$B_2H_6(g) \rightleftharpoons 2B(s) + 3H_2(g) \tag{2.20}$$