Development of Atomic Layer Deposition Processes for Nanotechnology Applications

Markus Bosund
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Abstract

This thesis focuses on atomic layer deposition (ALD) and its applications in nanotechnology. Two new low-temperature methods for the passivation of GaAs surfaces are presented and the film properties of the plasma ALD grown AlN are studied. A new deposition process for Yb₂O₃ thin films is developed and utilization of titanium dioxide films for photocatalytic applications is investigated.

The photoluminescence intensity of the near surface quantum wells (NSQWs) was used as an indicator for the passivation efficiency. The NSQW structures were coated by AlN or TiN. The AlN layer was deposited using plasma enhanced ALD whereas the TiN film was deposited using thermal ALD. Both coating methods increased the photoluminescence intensity significantly which indicated that the surface recombination rate of GaAs was clearly reduced. The coating layer thickness had a significant effect on the passivation efficiency.

The study of the influence of the process parameters on the PEALD AlN film properties revealed that the TMA and NH₃ plasma process led to stable film deposition. The growth temperature had the highest effect on the film impurity level: a higher temperature led to a lower hydrogen level. The NH₃ plasma pulse time did not have as significant effect on the atomic concentrations. The hydrogen level had an inverse correlation to the AlN film density and refractive index.

The developed growth process for the Yb₂O₃ films was based on the use of ytterbium β-diketonate (Yb(thd)₃) and O₂ precursors. The optimal growth temperature range was 300–350 °C, where the deposition rate was 0.18–0.20 Å/ cycle. The Yb/O ratio was 0.59 and 0.63 when the growth temperature was 300 and 350 °C, respectively. The impurity levels of H and C were 1.12, 0.65 at.%, in order.

The photodegradation of salicylic acid (SA) by TiO₂ was investigated. The TiO₂ thickness had a clear impact on the SA decomposition rate. A thin 3 nm thick layer did not cause photocatalytic activity. In the range of 3 to 50 nm the photodegradation rate increased and when the film was thicker than 50 nm the decomposition rate stayed relatively constant. The TiO₂ deposition temperature showed a clear effect on the film crystallinity and photodegradation rate. The fastest SA decomposition was observed when the TiO₂ growth temperature was 400 °C.

Keywords atomic layer deposition, plasma enhanced atomic layer deposition, GaAs passivation, photocatalyst, AlN, TiN, TiO₂

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Esseeväitöskirja

Tämä väitöskirja keskittyy atomikerroskasvatusmenetelmään ja sen nanoteknologisiin sovelluksiin. Työssä tutkittiin neljää eri sovellusalueetta, galliumarseniin pinnan passivointi, alumiininitrilikalvon fysikaaliset ominaisuudet, ytterbiumoksidin kasvatus ALD-teknikalla sekä ALD-titaanioksidin käyttö fotokatalyytisisissä sovelluuksissa.


Väitöskirjassa kehitettiin uusi ytterbiumoksidin ALD-valmistusprosessi. Prosessin lähdeaineet olivat ytterbium β-diketonaatit ja otsoni. Prosessin lämpötilaikuna oli välillä 300–350 °C, jossa kasvunopeus oli 1.18–0.20 Å/sylki. Ytterbiumin ja hapen atomaariset suhdeluvut (Yb/O) olivat 0.59 ja 0.63 kun reaktorilämpötilat olivat vastavasti 300 ja 350 °C. Kalvoista löytyi 1.12 % vetyä ja 0.65 % hiiltä.


atomikerroskasvatus, plasmahostettu atomikerroskasvatus, GaAs-passivointi, fotokatalyyysi, AlN, TiN, TiO2

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The greatest gratitude goes to my family. To my wife Suvi and sons Vilho and Onni.

Espoo, January 28, 2018,
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This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Properties of AlN grown by plasma enhanced atomic layer deposition”
For Publication I, the author optimized the aluminum nitride growth process, fabricated all the samples, measured and analyzed the films excluding the TOF-ERDA measurements and prepared the manuscript.

Publication II: “GaAs surface passivation by plasma-enhanced atomic-layer-deposited aluminum nitride”
For Publication II, the author developed the PEALD growth process for the aluminum nitride, deposited all the passivation layers, measured the EDX data and prepared the manuscript.

Publication III: “Atomic layer deposition of ytterbium oxide using β-diketonate and ozone precursors”
For Publication III, the author developed the ytterbium oxide growth process, fabricated all the samples, measured all the data excluding the TOF-ERDA measurements and prepared the manuscript.

Publication IV: “Passivation of GaAs surface by atomic-layer-deposited titanium nitride”
For Publication IV, the author developed the titanium nitride growth process, deposited all the passivation layers, measured and analyzed the XRR data and prepared the manuscript.
Publication V: “Atomic layer deposited TiO$_2$ films in photodegradation of aqueous salicylic acid”

For Publication V, the author optimized the titanium oxide growth process, deposited the TiO2 photocatalyst layers, measured and analyzed the XRR data.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>AlN</td>
<td>Aluminum nitride</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal oxide semiconductor</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DRAM</td>
<td>Dynamic random access memory</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at the half maximum</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared light</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>MCVD</td>
<td>Modified chemical vapor deposition</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro electro mechanical systems</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass flow controller</td>
</tr>
<tr>
<td>NSQW</td>
<td>Near surface quantum well</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>PEALD</td>
<td>Plasma enhanced atomic layer deposition</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>QW</td>
<td>Quantum well</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>SA</td>
<td>Salisylic acid</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>Titaniumtetrachloride</td>
</tr>
<tr>
<td>TiN</td>
<td>Titanium nitride</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TRPL</td>
<td>Time-resolved photoluminescence</td>
</tr>
<tr>
<td>TMA</td>
<td>Trimethylaluminum</td>
</tr>
<tr>
<td>TOF- ERDA</td>
<td>Time-of-flight elastic recoil detection analysis</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet light</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRR</td>
<td>X-ray reflectivity</td>
</tr>
<tr>
<td>Yb₂O₃</td>
<td>Ytterbium oxide</td>
</tr>
</tbody>
</table>
List of Symbols

A  
Mass of atom

A  
Acceptor

D  
Donor

E  
Energy

e  
Unit charge

$E_c$  
Conduction band energy

$E_g$  
Energy gap

$E_v$  
Valence band energy

$h$  
Planck constant

$\hbar$  
Reduced Planck constant

$k$  
Boltzmann constant

$n$  
Linear refractive index

$N_a$  
Avogadro constant

$r_e$  
Classical radius of electron

$T$  
Temperature

$V_b$  
Energy barrier height of quantum well

$V_c$  
Reduced energy barrier height of quantum well

$Z$  
Atomic number

$\beta$  
Absorption coefficient for X rays

$\delta$  
Dispersion coefficient for X rays

$\Delta f''$  
Imaginary part of dispersion coefficient for the X rays

$\Delta f'$  
Real part of dispersion coefficient for the X rays

$\theta$  
Reflected angle

$\lambda$  
Wavelength

$\rho$  
Mass density

$\tau$  
Photoluminescence lifetime of quantum well

$\omega$  
Angular frequency

$\omega$  
Diffracted angle
1. Introduction

Atomic layer deposition is a sequential thin film deposition method. ALD method was firstly introduced by Tuomo Suntola in the 1970s [1]. The first aim was to produce flat panel thin film electroluminescent displays [2, 3]. Miniaturization in the semiconductor industry has led to the requirement for atomic level thickness control, pinhole free thin films and high aspect ratios which have caused a huge growth in ALD technology. Recently ALD is mainly used e.g. in the gate oxide insulating layers in complementary metal oxide semiconductor (CMOS) devices [4–6], microelectromechanical system devices (MEMS) [7], OLED encapsulation [8], high-density dynamic random access memory (DRAM) [9], multilayer optical applications [10] and planar optical waveguides [11].

The main advantages of the ALD technology is the uniformity up to $m^2$ areas, low growth temperature, pin-hole free films [12] and high conformity [13]. ALD deposition process has also excellent film thickness control. The drawback of ALD is the low growth rate. It is possible to compensate the low growth rate by increasing the deposition area which leads to the fast volume growth.

A typical ALD reaction is based on two chemical precursors which are introduced into the reaction chamber separately. Reducing agents have also been used for lowering the process temperature, increasing the growth rate or improving the film purity [14, 15]. However, the use of reducing agents may also cause film impurities and the reactivity may be insufficient. Plasma enhanced ALD (PEALD) offers a way to activate the non-metal precursors using RF power. This means that the reactivity of the plasma enhanced precursors are not limited by thermal energy. By using plasma the process temperature can be lowered in some cases down to room temperature [16].

Gallium arsenide based technology is widely used in optoelectronics and
integrated circuits. The development of GaAs devices is partly limited by surface recombination and Fermi level pinning on the GaAs surface caused by surface oxidation and bond breaks. Therefore, the structures near the surface are unstable and suffer from a gradual degradation due to air and light exposure. Several surface passivation methods have been developed earlier but the difference with the ALD technology is the possibility to scale the process up easily and possibility to use relatively low passivation temperatures. ALD films are pinhole free which means that the ALD passivation layers work as a barrier which may improve the stability of the passivation.

Titanium dioxide (TiO$_2$) is widely used material in the purification of water and air [17, 18], construction materials [19], bacterial extermination [20], etc. When TiO$_2$ surface is radiated by an ultraviolet light it causes photoactivated surface which decomposes organic pollutants. The use of ALD for the TiO$_2$ surface coatings makes it possible to coat complex structures with an easy control for the film properties as crystallinity.

In this work, the growth parameters influence on the film quality in the case of PEALD AlN was studied in Publication I. Two GaAs passivation methods based on aluminum nitride and titanium nitride were investigated in Publications II and IV, respectively. In publication III the ALD growth process for ytterbium oxide based by ytterbium $\beta$-diketonate precursor and ozone precursors was developed. The motivation to develop an ALD growth process for ytterbium oxide was based on the optical telecommunication and high power fiber lasers. Optical fibers had earlier been doped using MCVD method and ALD offered alternative candidate for the doping because of conformality of the ALD growth. In the year 2012 Ponsoda et al. published an ytterbium fiber laser soot doping method which was combination of ALD and MCVD. This method led to the improved photodarkening resistivity compared to the earlier methods [21]. The suitability of the ALD grown TiO$_2$ for the photodegradation of salicylic acid was investigated in the publication V. This thesis was finished in the year 2017 and according the google scholar this article had been cited in 51 articles focusing on for example ALD TiO$_2$ photocatalytical activity [22]. Several water purification review articles also mention this publication [23, 24].

The structure of this dissertation consist of theory part where the theoretical background of the plasma discharges, atomic layer deposition technique, gallium arsenide surface states and quantum wells and photo-
chemical process of TiO$_2$ are discussed. In the chapter 3 the experimental
details of ALDs, PEALDs, X-ray measurement systems and photolumi-
nescence are introduced. The results are summarized in the chapter 3.
Finally, a conclusion about the studied topics are given.
2. Theory

2.1 Plasma ions and radicals

Plasma was introduced to describe ionized gas by Tonks and Langmuir [25]. From a scientific point of view, matter is often classified in terms of four states: liquid, solid, gaseous and plasma. More than 99% of the known universe is in the plasma state [26]. In brief, a plasma is a mixture of regular gas molecules, neutral particles, electrons and ions. Because of free electrons plasma is usually a good electrical and thermal conductor unlike neutral gas [27].

2.1.1 Plasma generation

Removal of the planetary electrons from the atoms of gas is called ionization. The ionization energy $U$ for typical deposition gases are: NH$_3$, 10.5 eV [28]; N$_2$, 15.7 eV [29, 30]; H$_2$, 15.6 eV [30]; O$_2$, 12.1 eV [29]; and Ar, 15.76 eV [31]. If gas is heated up to few thousand K the random kinetic energy of the molecules exceeds the ionization energy ($\frac{3}{2}kT > U$). After that the collisions strip electrons from the atoms forming a mixture of electrons, ions and neutral molecules. Because of the high temperature requirements of the process thermal plasma formation is not widely used in laboratory equipments. Second plasma formation method is to use high energy photons such as ultraviolet light or X-rays for the gas ionization [32]. That method is called photoionization process. The requirement for the photon is that the photon energy exceeds the plasma ionization energy ($\frac{hv}{\lambda} > U$). The third method for the plasma gas formation is the use of electric fields. The electric plasma discharges are classified as dc discharges, ac discharges and pulsed discharges [33]. Electrically coupled plasma is the most common plasma source in ALD, chemical vapor depo-
sition, sputters and reactive ion etchers.

### 2.1.2 Molecular collisions in a plasma

The basic operation of the plasma discharge is based on the high kinetic energy electron collisions with the neutral particles producing excited atoms, dissociated molecules, excited molecules and ions. The kinetic energy of the electrons is generated by an external electric field.

**Table 2.1.** Examples of particle reactions in a plasma based on ref [34]. A and B are atoms, A$^+$ and B$^+$ describe ions, A$^*$ and B$^*$ are atoms in a excited state and $\hbar\omega$ is a photon.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Process name</th>
</tr>
</thead>
<tbody>
<tr>
<td>a e + A → A$^+$ + 2e</td>
<td>Ionization</td>
</tr>
<tr>
<td>b e + A → A$^*$ + e</td>
<td>Excitation</td>
</tr>
<tr>
<td>c e + A$^-$ → A + 2e</td>
<td>Electron impact detachment</td>
</tr>
<tr>
<td>d A$^+$ + B → A + B$^+$</td>
<td>Charge transfer</td>
</tr>
<tr>
<td>e A$^*$ → A + $\hbar\omega$</td>
<td>Photoemission</td>
</tr>
<tr>
<td>f e + AB → A + B + e</td>
<td>Dissociation</td>
</tr>
<tr>
<td>g e + AB$^+$ → A + B$^*$</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>h e + AB$^<em>$ → A + B$^</em>$</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td>i e + AB → A + B$^-$</td>
<td>Dissociative electron attachment</td>
</tr>
</tbody>
</table>

Possible particle reactions in a plasma are listed in table 2.1. In the ionization process (a) electron collision removes an electron from an atom. Ionization process is possible also for two or multiatomic molecules. Electron collision with the atom or molecule can lead to elevation of the electron to an energy level above an arbitrary baseline energy state. This reaction is called excitation (b). Electron impact detachment (c) can be an important reaction in destroying negative ions. Two types of charge transfer reactions exist (d). If the two molecules have an exactly the same energy the reaction is called resonant charge transfer (such as O$^+$ + O). If the ionization potential is different it leads to nonresonant charge transfer. Example of the nonresonant charge transfer is O$^+$ and N reaction because the ionization potentials of O and N are different. The excited electron in the atoms or molecules can be recombined from the excited state to the ground state, thus producing photons. The wavelength of the photon is typically in the ultraviolet or visible range. The photoemission photons can be seen as a plasma glow. In the dissociation process (f) elec-
tron collision separates a two-atomic weakly reactive molecule into two reactive atoms which are called radicals. Radicals have a significant role in the material processing industry. Instead of forming two neutral radicals the electron collision with the two-atomic molecule can lead to the formation of a radical and an ion (g). The process is a combination of dissociation and ionization and therefore it is called dissociative ionization. An electron-ion pair can react producing an excited state atom and a radical (h). Negative ions can be generated by electron collision with the neutral molecule (i).

Table 2.2. Example of the reactions in a NH$_3$ [28, 35] and N$_2$ [36–38] plasma.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Process name</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ → NH$_3^+$ + e</td>
<td>Ionization</td>
</tr>
<tr>
<td>NH$_3$ → NH$_2^+$ + H + e</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>NH$_3$ → NH$^+$ + H$_2$ + e</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>NH$_3$ → NH$^+$ + 2H + e</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>NH$_3$ → NH$_3^+$</td>
<td>Excitation</td>
</tr>
<tr>
<td>N$_2$ + e → N$_2^+$ + 2e</td>
<td>Ionization</td>
</tr>
<tr>
<td>N + e → N$^+$ + 2e</td>
<td>Ionization</td>
</tr>
<tr>
<td>N$_2$ + e → N$^+$ + N + 2e</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>N$_2$ + e → N$_2^*$ + e</td>
<td>Excitation</td>
</tr>
</tbody>
</table>

The mixture of NH$_3$ and N$_2$ plasma is used in this work and therefore the examples of the particle reactions in the NH$_3$ and N$_2$ plasma are listed in table 2.2.

2.2 ALD and plasma ALD basics

![Figure 2.1](image)

Figure 2.1. ALD example cycle for Al$_2$O$_3$ deposition a) TMA precursor dose, b) purge, c) oxidant precursor dose, d) purge.
An example of the ALD growth cycle is shown in the Fig. 2.1 a). Precursor molecule A reacts with the surface producing by-product molecules, b) substrate is covered by precursor molecules and non-reacted chemicals and by-products are purged from the reactor, c) precursor B reacts with the surface and d) precursor B and by-products are purged. One monolayer is now produced. This entire reaction is called the ALD cycle.

### 2.2.1 ALD reactors

As in any chemical reaction the reaction temperature plays important role in the ALD process. The temperature range where the ALD process fulfills the requirements of the self-terminating reactions is called the ALD temperature window. This temperature range is unique for each precursor chemical. Temperature also has a strong effect on the deposi-
tion rate which means that a uniform temperature is required in order to deposit uniform films. In hot wall reactors the substrate holder and reactor walls are kept at uniform temperature [39]. In cold wall reactors the substrate is heated separately while the reactor walls are kept cold or at a lower temperature than the substrate.

The uniformity, conformality, precursor efficiency and deposition rate play a significant role in the ALD applications. Therefore, several ALD reactor concepts have been developed. The schematic of a cross-flow ALD reactor is shown in Fig. 2.2 a [40]. The reactor volume is reduced by bringing the top of the reactor near to the bottom where the substrate is kept. The multiple substrate version of the cross-flow reactor called batch reactor is shown in Fig. 2.2 b). The working principle of the batch reactor is similar with the cross flow but instead of one substrate a stack of several substrates is used. The roll-to-roll reactor (Fig. 2.2 c) is used for flexible substrates which can be rolled from a roll to the other through the separated precursor gas zones [41]. In the showerhead reactor shown in Fig. 2.2 d) the precursor gas is directed through the showerhead on to the substrate. Showerheads are also used in the batch reactors to distribute an equal precursor flow and dose onto the substrates. In the reactors a, b and d a constant inert carrier gas flow is directed through the reactor and the precursors are mixed to the carrier gas flow. An ALD reactor can also be equipped with two valves as shown in Fig. 2.2 e). These valves can be closed after a precursor is pulsed in to the reactor. This reactor type is called stop flow ALD. The benefit is that the residence time of the precursors can be increased. Long dwell time helps the molecules to diffuse in the high aspect ratio substrates and it also allows more reaction time for the precursors if the reaction is slow. If the stop flow valves are installed outside of the heated area the precursors may condensate in to the valves which leads to valve leak or blockage. To avoid that the valves are usually installed in to the heated zone but in that case the reaction temperature is limited to the maximum temperature of the valves. A schematic of a rotating susceptor ALD reactor is shown in Fig. 2.2 f). The precursor molecules are directed to the precursor zones which are separated from the each other by an inert gas. The substrate travels between the precursor zones [42, 43]. This ALD reactor type is also called spatial ALD. Although the commercial spatial ALD reactor is a relatively young concept compared to the cross flow reactor the rotating substrate was used in the earliest ALD reactors in 1974 [44]
2.2.2 Precursor pulsing

Solid, liquid and gaseous precursors are used in thermal ALD. Gaseous precursors can be pulsed into the reactor through an ALD pulse valve. The schematic of the most common ALD precursor containers and lines is shown in Fig. 2.3 a. That kind of containers are used for liquid and solid precursors. The container can be heated up so that the vapor pressure of the precursor chemical exceeds the reactor pressure. The precursor is pulsed into the reactor by opening the valve 2 as shown in Fig. 2.3 b. Some precursors do not have sufficient vapor pressure or the stability of the precursor suffers from the heating. In that case it is also possible to pulse inert gas like N$_2$ or Ar into the precursor container by opening the valve 1. That increases the container pressure so that when the valve 2 is opened the precursor drifts into the reactor. Another example of the ALD precursor pulsing is shown in the Fig. 2.3 c. Inert gas is directed into the precursor line. The gas flow finds two routes 1) towards the reactor and 2) towards the precursor. The gas flow towards the precursor prevents the precursor flow into the reactor. It works like a valve. Therefore, this pulsing method is called inert gas valving. The precursor can be pulsed into the reactor by opening the valve 3 as shown in the figure d. The gas flow through that valve is greater than the inert gas valving flow. That turns the flow towards the reactor and the precursor is drifted into the reactor with the carrier gas. Although the valve type a is more common in the ALD systems the inert gas valving is also used. Some ALD equipment manufacturers are using combination of both valving methods in the same precursor line.

2.2.3 Plasma enhanced ALD

The use of plasma in ALD technology is based on several reasons. The speed of the chemical reactions depends on the temperature. In certain ALD processes low temperature leads to incomplete reactions which can cause impurities [45] or low growth rate [46]. Low reaction temperature may still be crucial for many applications. Plasma also makes it possible to develop processes which are not available in the thermal ALD. One example of that is the aluminum nitride growth process using trimethylaluminum (TMA) and ammonia (NH$_3$) precursors. Self-limiting ALD deposition can not be achieved because a practical growth rate is only achieved at the temperatures where the TMA decomposition takes place [47]. When
Figure 2.3. Precursor dosing into the ALD reactor a) prevented by an ALD valve, b) dosing by an ALD valve, c) prevented by the inert gas valving, d) dosing by the inert gas valving.

the NH₃ is activated by the plasma the minimum growth temperature is as low as 150 °C as shown in the publication I in this thesis. The growth rate of an ALD process can also be increased by plasma [48]. The use of plasma has a clear effect on the film properties. One example of that is the passivation of solar cells by ALD Al₂O₃. The PEALD grown Al₂O₃ decreases the surface recombinations more compared to the thermal ALD Al₂O₃ based on water as an oxidizer [49]. Plasma can also affect to the crystallinity of an ALD film [50]. Only non-metal precursors can be enhanced by plasma. Metal precursor dissociation by plasma leads to the non-saturative CVD growth and therefore the plasma discharge must be turned off during the metal pulse.

Plasma radicals and ions have several functions in the PEALD cycle. The residues of the carrier molecules can be removed from the surface using plasma radicals. One example of an impurity atom is chlorine which originates from the metal chloride precursor (MCl). In that case hydrogen radicals can be used to extract Cl from the surface [51] producing gaseous HCl. This process can improve the reactivity of the surface species and decrease the Cl level in the film. Plasma radicals can be also used as oxygen or nitrogen sources because of their high reactivity. An example
of the chemical reaction of the H/N plasma where the surface chlorine is removed and nitridated by radicals is presented in eq. 2.1 [52, 53].

\[
\text{MCl}_x + H + N \rightarrow \text{MCl}_{x-1}N + \text{HCl.}
\] (2.1)

PEALDs can be divided into direct plasma ALD (DPALD) and remote plasma ALD (RPALD). The basic feature of DPALD is that the substrate is kept in the plasma discharge or very close to it which leads to the bombardment of the charged particles in to the substrate. Higher ion and radical flow can be reached by DPALD but the downside is that the ion bombardment may damage the substrate leading to the impurities and defects [54]. When considering plasma damages it is important to separate two factors 1) energy of the plasma ions 2) amount of the ions. The lifetime of the plasma radicals is much longer compared to the lifetime of the charged particles [55]. If the plasma discharge and the substrate have a clear distance between them the plasma radicals can reach to the substrate in pursuance of ions and electrons are found only from the plasma discharge. Therefore, RPALD technology is also called radical ALD. However, ion drift to the substrate in the case of remote plasma ALD has been reported [56].

**Figure 2.4.** Schematics of the a) inductively coupled plasma, b) capacitively coupled direct plasma and c) capacitively coupled remote plasma ALD.

The schematic of an inductively coupled remote plasma ALD is shown in Fig. 2.4 a. The plasma discharge is generated inductively across a dielectric, e.g., a glass tube. Radicals can drift on the substrate when the plasma power is on. The metal precursor is pulsed in to the reactor when
the plasma power is turned off. The frequency of the RF power is usually 13.6 MHz. Instead of a RF source also microwaves can be used for the discharge formation. High plasma density can be generated inductively [34] but the distance from the discharge to the substrate is relatively long which decreases the amount of radicals which can reach the substrate. The schematics of the capacitively coupled direct plasma ALD is shown in Fig. 2.4 b. The plasma discharge is generated between two conductive capacitor plates by RF voltage. The lower capacitor plate is the susceptor. The advantage of this structure is that the distance from the plasma discharge to the substrate is constant and does not depend on the substrate area. Therefore, the process can be scaled up for the industrial use. The drawback is that in the direct plasma the plasma ions can damage the substrate. The ion bombardment can be eliminated by adding a grounded plate or grid between the substrate and the upper plate as shown in Fig. 2.4 c). This PEALD system is called capacitively coupled remote plasma ALD. Part of the plasma energy generates heat which means that the use of plasma can increase the reactor temperature during the PEALD deposition.

2.3 Near surface quantum wells and surface passivation

In this thesis NSQWs were used in Publications II and IV as test structures to study the surface passivation of GaAs by ALD thin films.

QWs are used for example in light emitting diodes (LED) [57, 58], semiconductor lasers [59] and light detectors [60]. A QW structure consists of a semiconductor material such as InGaAs sandwiched between mate-
rial layers with a wider bandgap such as GaAs. The quantum effects take place when the thickness of the quantum well is less than de Broglie wavelength of the charge carriers. The light emitting process is based on electrically or optically induced carrier excitation over the semiconductor band gap. Excited electron hole pairs can recombine in the quantum well. This recombination produces a photon, thus the recombination type is called radiative recombination.

The dynamics of the carrier processes in a GaAs/InGaAs/GaAs quantum well are shown in Fig 2.5. In this work optical excitation by photons was used to generate electron-hole pairs. The carriers drift in to the InGaAs QW and recombine radiatively as a type I recombination. In the case of NSQW type II non-radiative recombination process also occurs on the GaAs surface [61]. This surface recombination takes place if the distance from the QW to the surface is less than 20 nm. The surface recombination is caused by GaAs surface states. The luminescence intensity of the NSQW is sensitive to the number of the surface states. The higher the density of surface states, the lower the radiative type I recombination rate and the weaker the luminescence intensity. In this work for example an AlN passivation layer was grown on the NSQW which decreased the number of type II recombinations and led to a higher radiative recombination rate. That was seen as an increased luminescence intensity of the NSQW.

2.4 TiO$_2$ photocatalysis

The photocatalytic reaction is based on the interaction of ultraviolet light with the surface material leading to surface reactions. The main requirements for the photocatalytic materials are: chemically and biologically inert, photocatalytically active, easy to produce and use, activated by sunlight and low cost. TiO$_2$ displays all the desired features with the exception that it does not absorb sunlight effectively [62]. The commercial photocatalytic applications can be divided in to three modes of action: photomineralization (PCO), photo-sterilization and photoinduced super hydrophilicity (PSH) [63]. Some application areas are: water and air purification [17, 18], self-cleaning construction materials [19, 64] and antibacterial coatings in prosthesis [20]. Three crystal structure forms of TiO$_2$ exist: anatase, rutile and brookite. In addition, an amorphous phase is possible. The anatase crystal structure appears to be the most desired be-
cause of the strongest photocatalytical activity [63]. Several TiO$_2$ growth methods have been developed e.g. chemical vapor deposition [65], sol-gel method [66], sputtering [67] and spin coating [68]. The benefit of the ALD use is the possibility to coat large surface areas up to m$^2$ scale. The crystallinity of the film can also be controlled by controlling the growth temperature. The growth is also highly conformal on complex structures.

The photochemical process of TiO$_2$ is based on the electron hole pair generation by photons. The photon energy must be higher than the band-gap energy of the TiO$_2$ ($E_g < \hbar \omega$) which is in the range of 3.0-3.2 eV. Therefore, the wavelength of light must be less than 413 nm.

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![Figure 2.6. Band diagrams of the photocatalysis process on TiO$_2$ surface.](image)

The photocatalytic reaction process is presented schematically in Fig 2.6. The photon generates an electron-hole pair and the electrons and holes can diffuse to the surface where electrons can reduce acceptors (A) and holes can oxidize donors (D). The overall reaction can be written as [63]

$$A + D \rightarrow A^- + D^+.$$  \hspace{1cm} (2.2)

One well-documented practical example of the photomineralization process by oxygen can be written following way [69]

$$\text{organic} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{mineral acids}. \hspace{1cm} (2.3)$$

This process requires semiconductor substrate and light ($E_g < \hbar \omega$).
Theory
3. Experiments

This chapter introduces the experimental methods of sample fabrication and characterization used by the author of this thesis. Section 3.1 describes the atomic layer deposition and plasma enhanced atomic layer deposition equipments. In section 3.3 X-ray diffraction and reflectivity measurement systems are described. Section 3.4 introduces the photoluminescence measurement setup. The other characterization techniques used in the thesis include time-of-flight elastic recoil detection analysis (TOF-ERDA) to measure the atomic concentrations from the ALD grown films in publications I and III. A Philips Plasmos SD 2300 laser ellipsometer operating at 632.8 nm was used in a clean room environment to determine the thickness and uniformity of the deposited films in publications I and III.

3.1 Thermal atomic layer deposition

The Yb$_2$O$_3$ films in Publication III were grown by a commercial Beneq TFS 500 ALD apparatus equipped with self-made tube shaped aluminum reactor with a diameter of 24 mm and length of 23 cm. Photos of the ALD system and the tube reactor are shown in the Fig. 3.1. The ALD tool was equipped with HS-200 hot source. The schematic of the ALD apparatus is shown in Fig. 3.2.

The TiN films in Publication IV were deposited using TiCl$_4$ and NH$_3$ as the precursors. TMA was used as a reducing agent between the TiCl$_4$ and NH$_3$ pulses. The reaction temperature was 275 °C. This process had earlier been published by Juppo et al. [70].
3.2 Capacitively coupled PEALD and AlN processes

The growth of AlN films for Publications I and II was executed using a commercial Beneq TFS 500 capacitively coupled remote plasma ALD equipped with Advanced Energy Cesar (13.56 MHz) RF power supply and VarioMatch matching box. Capacitively coupled plasma head was integrated on the top of a cross flow reactor. The working principle of the cross flow reactor is explained in Chapter 2.2.1.

The schematics of the PEALD reactor used in this work is shown in Fig. 3.3 (upper). The plasma discharge region was above the sample. The ion drift to the substrate was prevented by a grounded grid which located between the plasma discharge and the substrate. A constant nitrogen gas flow was directed through the plasma discharge. Nitrogen flow was also directed from the precursor line which locates on the left in Figure 3.3. The pulsing technique is described in Fig 3.3 (lower). The PEALD cycle consists of the following steps: 1) TMA pulse, 2) N\textsubscript{2} purge, 3) plasma on, 4) NH\textsubscript{3} pulse, 5) plasma off, 6) N\textsubscript{2} purge.

3.3 X-ray reflectivity and diffraction

X-ray reflectivity (XRR) measurement was used in film thickness determination, mass density determination and surface roughness determination.
in the publications I-V. XRR is a non-contact measurement method which can be used for the determination of thin film thickness, mass density and surface roughness. Philips Xpert Pro diffractometer apparatus was used in this thesis. The schematics of the setup is shown in Fig. 3.4. The measurement assembly consist of Ni and Cu attenuators, an X-ray mirror, a Soller slit (2.29°) and a divergence slit with a 1/32° deg fixed aperture at incident beam setup. The reflected beam is collected using a thin film collimator, a 2.29° Soller slit, a flat graphite crystal monochromator and a scintillation detector assembly.

The refractive index for the X-rays can be determined as a complex number:

\[ n = 1 - \delta - i\beta \]  
(3.1)
where dispersion $\delta$ and absorption coefficients $\beta$ are defined as

\[
\delta = \frac{N_a r_e (Z + \Delta f') \rho \lambda^2}{2\pi A},
\]

(3.2)

\[
\beta = \frac{N_a r_e \lambda^2 \rho \Delta f''}{2\pi A},
\]

(3.3)

where $\lambda$ is the wavelength of the X-rays, $r_e (= 2.818 \times 10^{-15} \text{ m})$ is the classical radius of the electron, $N_a$ Avogadro constant, $Z$ atomic number, $A$ mass of atom, $\rho$ mass density of the material, $\Delta f'$ and $\Delta f''$ are real and imaginary parts of the dispersion coefficients for the specific material [71, 72]. When the refractive index is defined for the X-rays, the reflectance curve can be calculated using Fresnel’s equations leading to the Parratt’s [73] formalism

\[
r_{j-1} = \frac{F_{j-1} - 1 + r_j e^{-2k_j t_j}}{1 + F_{j-1} r_j e^{-2k_j t_j}},
\]

(3.4)

where $t_j$ is the thickness of the $j$:th layer. The factors in Equation 3.4 are defined as

\[
q_j = \frac{4\pi f_j}{\lambda},
\]

(3.5)

\[
F_{j-1} = \frac{k_{j-1} - k_i}{k_{j-1} + k_i},
\]

(3.6)

\[
k_j = \frac{2\pi}{\lambda} \sqrt{\theta^2 - 2\delta_j - 2i\beta_j}.
\]

(3.7)

Interface roughness can be modelled using Nevot-Croce approximation [74] replacing the $F_j$ in the Equation 3.4 by

\[
\tilde{F}_j = F_j e^{-2k_j k_{j+1} \sigma_j^2},
\]

(3.8)

Where the $\sigma_j$ is the root mean square of the interface roughness of the $j$:th surface.
3.4 Photoluminescence spectroscopy

The passivation efficiency in the NSQWs were analyzed with the photoluminescence (PL) method. In a PL measurement, electron-hole pairs are generated by excitation light. The energy of the excitation photon must be above the band gap energy of the measured semiconductor material. In this work 532 nm wavelength was used for the excitation. The electrons and holes recombine in the sample structure. The recombination process can be radiative or nonradiative recombination. Radiative recombination produces photons which can be measured.

**Figure 3.5.** Schematic illustration of a) photoluminescence and b) time resolved photoluminescence setups used in this work.

A schematic picture of the PL measurement system is shown in Fig. 3.5a.
The measurement setup consist of the Nd:YVO$_4$ excitation laser ($\lambda=532$ nm). The sample was located in a helium cryostat. The cryostat temperature was kept at 9 K. The luminescence light from the sample was collected by collimating and focusing lenses through the monochromator to the detector. A lock-in amplifier with a chopper was used to improve the signal-noise ratio. The measured data was recorded with a computer.

The time-resolved photoluminescence (TRPL) measurement schematics is presented in Fig. 3.5 b. A mode-locked titanium sapphire laser operating at the 800 nm wavelength was used to generate 150 fs pulses. The PL transients at chosen wavelengths were detected by a Peltier-cooled microchannel plate photo-multiplier and time-correlated single photon counting electronics.

### 3.5 Fabrication of near surface quantum wells

![Figure 3.6. Schematic diagram of the MOVPE system.](image)

Near surface quantum wells (NSQW) were manufactured using commercial Thomas Swan Scientific Equipment metal organic vapor phase epitaxy (MOVPE) reactor. A schematic diagram of the system is shown in the Fig. 3.6. Trimethylindium (TMIn), trimethylgallium (TMGa), tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP) were used as sources of indium, gallium, arsenic and phosphorus respectively. The vapor pressure of the precursors was controlled by temperature-controlled baths. Hydrogen was used as the carrier gas. The precursor flow rates were controlled by mass flow controllers (MFCs). Group III and V precursors were fed through separate lines to prevent reactions in the precursor lines. Pyrolysis furnace was used to decompose the toxic non-reacted precursors. Toxic residual reaction molecules were absorbed by a
gas scrubber which located in the exhaust line. The substrate was placed on $2 \times 2 \text{ cm}^2$ graphite susceptor which was heated by a halogen lamp. The actual substrate temperature was approximately $50 \ ^\circ\text{C}$ lower than the thermocouple reading. The reason for that was the cooling effect caused by the gas flow thorough the reactor. The temperatures mentioned in this work are thermocouple readings.

Semi-insulating GaAs (100) substrates were coated by an epitaxial buffer layer on top of which a $4-4.3 \text{ nm}$ thick In$_{0.21}$Ga$_{0.79}$As quantum well was grown. A GaAs capping layer with a thickness of $2-6 \text{ nm}$ was grown on top of the quantum well. The NSQW structure was passivated using ALD. The possible process variations between the separate MOVPE depositions were eliminated by growing one sample and cleaving it to several pieces. One was kept as a reference sample while the others were used in the passivation experiments. In that way, all the samples and the reference in one thickness series originated from the same MOVPE deposition.

---

**Figure 3.7.** Schematics of the NSQW structure.
4. Results and Discussion

4.1 The properties of PEALD AlN

This chapter discusses the results of Publication I where the physical properties of the PEALD grown AlN films were investigated. The effects of the growth and plasma parameters on the atomic concentrations, refractive index, mass density and crystallinity are reported.

4.1.1 Effect of plasma discharge time

![Figure 4.1. AlN film thickness as a function of the NH3 plasma time.](image)

Figure 4.1 presents the film thickness as a function of plasma power. The growth saturated when the plasma time was longer than 15 s. The required time for the saturation depended only slightly on the plasma power. Only minor growth rate increasement was seen when the plasma time was doubled from 15 to 30 s with 60 W plasma power. The plasma power had a clear effect on the deposition rate. This behaviour is in agreement with the results published by Liu et al. [46].
Results and Discussion

The effect of the NH$_3$ plasma pulse length on the atomic concentrations in the AlN film is shown in Fig 4.2. The plasma power was 200 W and the deposition temperature 200 °C. Nitrogen concentration increased slightly whereas the hydrogen concentration decreased when the plasma pulse length was increased from 2.5 to 15 s. The pulse time lengthening from 15 to 30 s did not decrease to the H concentration. It can be seen in Fig. 4.1 that the saturation time for the reaction was 15 s and only minor changes were achieved by lengthening the plasma pulse time more. Carbon impurities were originating from the TMA precursor. The C level stayed in the range of 2.3 to 2.5 % and the plasma pulse time didn’t have a strong influence on that. Oxygen impurities in the range of 0.07 to 0.25 % were found from the film. The samples had been stored in the ambient air which explains the presence of the O impurities. Another possible source for the minor oxygen impurities is the carrier gas or ammonia. In this work the gas purity was better than 99.9999 %.

4.1.2 The effect of the deposition temperature

The deposition temperature had a clear influence on the deposition rate and atomic concentrations as one can see from Fig. 4.3. The growth rate increased from 0.56 to 1.32 Å/cycle in the growth temperature range of 100 to 300 °C. The film grown at 100 °C had a very high oxygen contamination level and very low nitrogen concentration. At the same time it had the lowest Al concentration of about 20 %. From these results it can be concluded that deposition at 100 °C led to non-stabile or non-stoichiometric film growth. Because of that the film was oxidized in the ambient air unlike the film grown at 150 °C or higher temperature. When the deposition temperature was 150 °C or higher, the film was stabile in ambient
Figure 4.3. Growth rate and atomic concentrations of the AlN film as the function of the growth temperature.

air. The observed significant hydrogen impurity concentration was found to decrease when the growth temperature was increased, probably due to incomplete removal of NH₅-species from the surface. It has been shown earlier that the TMA and NH₅ surface reaction efficiency depends on the growth temperature [75, 76] which is in good agreement with this work. It also makes sense to assume that the NH₅ species in the ammonia plasma does not remove the NH₅ species from the surface. This also explains the deposition rate dependency on the growth temperature in Fig 4.3.

4.1.3 Physical properties of the film

The deposition temperature had a clear effect on the film properties. The density of the film increased from 2.4 to 2.8 g/cm³ when the deposition temperature was increased from 150 to 300 °C. The refractive index at 633 nm wavelength was 1.844 and 1.976 for the growth temperature of 150 and 300 °C, respectively. The XRD measurement revealed an AlN (200) diffraction peak for the film grown at 300 °C. However, no XRD peaks were found for the samples grown at lower temperatures which indicates that the films were amorphous. When these results were compared to the atomic concentrations data shown in Figure 4.3 it was concluded that the hydrogen concentration had a strong effect on the film quality. High H concentration decreased both the refractive index and the density of the film. The refractive index of the AlN film is relatively easy to measure by an ellipsometer. It can be used as an indicator of the film purity based on the results shown in Publication I Fig. 10.
4.2 Yb$_2$O$_3$ Growth

Novel ALD method using ytterbium beta-diketonate (Yb(thd)$_3$) and ozone (O$_3$) precursors for growing Yb$_2$O$_3$ was presented in the Publication III. The deposition temperature range from 250 to 400 °C was investigated. The evaporation temperature for the Yb(thd)$_3$ was 170 °C.

4.2.1 Yb$_2$O$_3$ growth process

![Graph](image)

**Figure 4.4.** Growth rate (left) and thickness variation (right) as a function of pulse length of a) Yb(thd)$_3$ and b) O$_3$.

The growth rate and thickness variations as a function of the pulse length are shown in Fig. 4.4. ALD-like saturative growth rate was observed for both Yb$_2$O$_3$ and O$_3$ when the pulse time was 0.6 s and 3.0 s respectively. The thickness variation was determined from 2 cm x 12 cm Si(100) substrates. The variation stayed below 2% in the saturation conditions. The temperature window for the ALD growth was 300-350 °C under which conditions the growth rate was 0.15 Å/cycle. Lower growth temperature led to a significantly lower growth rate caused by self-limitations due to slow reactions. When the temperature was 400 °C the growth rate decreased to 0.1 Å/cycle and the thickness variations increased significantly. This was caused by the decomposition of Yb(thd)$_3$. 
4.2.2 Yb<sub>2</sub>O<sub>3</sub> film properties

The deposition temperature had an influence on the film properties. The O/Yb ratio changed from 0.59 to 0.63 when the growth temperature was increased from 300 to 350 °C. The O/Yb ratio of the fully stoichiometric Yb<sub>2</sub>O<sub>3</sub> is 0.67 which is relatively close to the value for the film grown at 350 °C. Carbon impurities, originating from the Yb(thd)<sub>3</sub> molecule, were found from the film. When the reactor temperature was 300 °C the carbon concentration was 1.4%. Raising the temperature to 350 °C led to 0.65 % C concentration. The hydrogen impurity concentration was 2.0% and 1.12 % when the deposition temperature was 300 and 350 °C, respectively. The TOF-ERDA measurement indicated that minor quantities of nitrogen were also present in the film. The total nitrogen concentration was lower than 0.1 %. The only explanation for the nitrogen residues was N<sub>2</sub> used as the carrier gas. According to the X-ray diffraction the film was polycrystalline and the following Yb<sub>2</sub>O<sub>3</sub> crystal orientations were measured from the films: (222), (400), (411), (440), (611) and (622). The observed XRD peak positions were in good agreement with the earlier results [77–79].

The deposition temperature and the type of the substrate had a clear effect on the XRD peak heights. When a glass substrate was used the (400) orientation gave the strongest XRD peak and the intensity of the (222) peak was low. When the films were grown on Si(100) substrates at 350 °C the (222) peak was almost as strong as the (400) peak. X-ray reflectivity measurements indicated that the mass density of the film was 8.9 and 9.0 g/cm<sup>2</sup> when the growth temperature was 300 and 350 °C, respectively. Derenzo et al. [80] had earlier measured the density of the Yb<sub>2</sub>O<sub>3</sub> film. In that study the density was 9.2 g/cm<sup>2</sup> which was slightly higher compared to this work. This difference can be explained by small differences in the crystal structures. The optical properties of the Yb<sub>2</sub>O<sub>3</sub> films were investigated using a near infrared spectroscopic ellipsometer. The refractive index was 1.86-1.89 at the 800-1600 nm wavelength. The growth temperature had only a weak effect on the refractive index. The refractive index variation within the sample was lower than 1 %. The surface morphology was studied using atomic force microscope. The deposition was agglomeration free. The RMS roughness of the film was lower than 1.3 nm.
4.3 GaAs surface passivation

This chapter discusses the research observations presented in Publications II and IV. A GaAs surface was passivated using two different ALD processes. In Publication II thin AlN passivation layers were deposited on near surface quantum wells using plasma enhanced ALD technique. In Publication IV, the suitability of GaAs surface passivation by using an ALD grown TiN layer was investigated.

4.3.1 Photoluminescence intensity

![Figure 4.5. Photoluminescence intensity of a) AlN and b) TiN passivated NSQWs.](image)

The maximum PL intensity of the AlN passivated NSQWs as a function of the passivation layer thickness is shown in Fig. 4.5 a). The samples with zero AlN layer thickness are uncoated reference samples. The PL intensity values of the AlN passivated NSQWs were normalized so that the intensity of the deep QW was set to 100. The highest 29 times intensity improvement was observed when the GaAs capping layer thickness was 6 nm and the AlN passivation layer was 0.5 nm. When the passivation layer was thicker the PL intensity saturated to a level approximately an order of magnitude higher compared to the unpassivated reference NSQW. When the GaAs capping layer was 4 nm the PL intensity maximum value was found when the AlN layer thickness was 0.3 nm. When the thickness of the AlN was 2 nm or more no PL intensity was observed from the NSQWs.

The maximum PL intensity of the TiN passivated NSQWs is shown in Fig. 4.5 b). The PL intensity of the NSQWs was normalized so that the PL intensity of the unpassivated reference NSQW was set to 1. The capping layer thickness had a similar effect on the PL intensity as in the case of the AlN passivation. In the case of TiN the highest PL intensity was
found when the thickness of the passivation layer was 4 nm. The PL intensity was approximately 15 times higher compared to the unpassivated reference. When the capping layer was 3 nm an order of magnitude improvement to the PL intensity was achieved. The NSQWs with the 3 nm cap were measured again after one month to find out the stability of the passivation method. It was found out that thin 1-3 nm TiN layers did not protect the sample as well as the 4 nm coating. The most probable reason for this was the oxidation of the GaAs surface through the thin TiN layer.

The suitability of $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ for the NSQW passivation was also tested. In our tests it came out that $\text{Al}_2\text{O}_3$ or $\text{TiO}_2$ film coating dropped the PL intensity of the NSQWs to zero in all cases. When the $\text{Al}_2\text{O}_3$ film was removed by hydrofluoric acid the PL intensity of the NSQWs recovered. Therefore, it was reasonable to assume that instead of reducing the surface recombination rate the oxide layers increased it. This was in good agreement with earlier results indicating that the oxygen bonds on the GaAs surface increase the density of surface states [81, 82].

### 4.3.2 The luminescence lifetime of the passivated NSQWs

**Table 4.1.** The PL lifetime ($\tau$) of the TiN and AlN passivated NSQWs. The capping layer thickness of the passivated NSQWs is 3 and 4 nm for TiN and AlN respectively.

<table>
<thead>
<tr>
<th>Passivation film</th>
<th>Thickness (nm)</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN (ref.)</td>
<td>-</td>
<td>0.31</td>
</tr>
<tr>
<td>TiN</td>
<td>2.0</td>
<td>0.44</td>
</tr>
<tr>
<td>TiN</td>
<td>2.9</td>
<td>0.44</td>
</tr>
<tr>
<td>TiN</td>
<td>3.9</td>
<td>0.42</td>
</tr>
<tr>
<td>TiN</td>
<td>5.6</td>
<td>0.43</td>
</tr>
<tr>
<td>TiN (deep QW ref.)</td>
<td>-</td>
<td>0.51</td>
</tr>
<tr>
<td>AlN (ref.)</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>AlN</td>
<td>0.1</td>
<td>0.24</td>
</tr>
<tr>
<td>AlN</td>
<td>0.3</td>
<td>0.74</td>
</tr>
<tr>
<td>AlN</td>
<td>0.5</td>
<td>0.68</td>
</tr>
<tr>
<td>AlN</td>
<td>1.0</td>
<td>0.59</td>
</tr>
<tr>
<td>AlN</td>
<td>1.9</td>
<td>1.34</td>
</tr>
<tr>
<td>AlN (deep QW ref.)</td>
<td>-</td>
<td>1.20</td>
</tr>
</tbody>
</table>

The PL lifetime results of the NSQWs and reference QWs are summarized in Table 4.1. One can see that the lifetimes of the deep QWs were
different in the case of TiN and AlN passivation. This difference was caused by the slightly different quantum well samples. Because of that it was not possible to accurately compare the lifetimes of the TiN and AlN passivated NSQWs.

The TiN passivation increased the PL lifetime by approximately 42%. Unlike the PL intensity, the lifetime did not depend on the TiN layer thickness when the TiN layer thickness was in the range of 4-6 nm. According to Dreybrodt et al. the PL lifetime of NSQW depends directly on the PL intensity [61]. That was not in agreement with this study where the intensity depended strongly on the TiN thickness while the PL lifetime stayed constant. Possible explanation for that was the PL light reflection from the GaAs/TiN boundary.

The lifetime did not increase linearly as a function of the AlN thickness. The lifetime followed the PL intensity when the AlN thickness was less than 0.6 nm. After that the lifetime increased. The highest lifetime was achieved when the AlN thickness was 1.9 nm. The lifetime was even longer than the lifetime of the deep QW which was the theoretical maximum for a QW [61] because surface recombination does not occur in the deep QWs. Therefore, the presence of third carrier transition mechanism needed to be proposed. The first explanation was that the GaAs surface (capping layer) was nitridated by the NH$_3$ plasma which led to the formation of GaAsN$_x$ which decreased the conduction band minimum. In that way a carrier trap formed on the GaAs/AlN interface. The second explanation was that the insulating GaAs layer acted as a carrier trap on the GaAs/AlN surface. Trapped carriers can recombine through the QW which increases the lifetime.

4.3.3 PL peak position

Both passivation methods caused shifts in the QW PL peak energy position. In the case of TiN the effect was random and the PL peak shifts were observed to change in the range of 10 meV. In the case of AlN a clear redshift of the PL peak was observed in all the passivated samples. The largest redshift values were detected from the sample which also had the highest PL intensity.

The PL curves of AlN passivated NSQWs and references are shown in Fig. 4.6. The deep quantum well (curve a) had the same peak position as the NSQW (curve b) but the intensity of the deep QW was approximately 50 times higher. Curve c is the AlN passivated NSQW which had the
Results and Discussion

Figure 4.6. PL spectra of (a) deep quantum well, (b) unpassivated NSQW, (c) NSQW with 0.5-nm-thick AlN coating (d) the same sample as in c after HF etching and (e) NSQW with a 1.9-nm-thick AlN coating.

highest PL intensity. It can be seen that the PL peak had redshifted as much as 41 meV. When the AlN layer was removed by dipping the sample in to the hydrofluoric acid the PL peak blueshifted but not to the original level. Also the PL intensity dropped to the same level with the unpassivated reference. This was a clear evidence that the AlN layer caused the PL intensity increase and redshift. However, some residue effect of the passivation treatment had stayed even after the AlN removal. The result of 1.9 nm thick AlN layer passivation is shown in the curve d. Both PL intensity increase and redshift were weaker compared to the curve c.

Figure 4.7. Schematics of the layer structure used in the simulations.

The reason for the redshift was investigated. The first explanation was the nitridation of the GaAs surface which led to the conduction band drop. The reduced height of the potential barrier in the capping layer decreased the QW energy levels. Upper limit estimation for that were simulated using the NSQW structure shown in Fig. 4.7. The energy levels of the QW
were simulated while decreasing the barrier height of the capping layer \( V_c \) from the original barrier height \( V_b = 158 \text{ meV} \) to \( \frac{1}{2} V_b \). The capping layer thickness \( d \) was set to 6 nm. The Schrödinger equation was numerically solved using the Finite difference method. In the simulations it came out that the redshift of the QW energy level would only have been 15 meV which did not explain the 41 meV redshift. Another explanation for the redshift of the PL peak was based on the earlier research done by Moison et. al. [83] where the PL spectra of GaAs/GaAlAs NSQWs had been studied. In that paper a strong up to 40 meV redshift where the PL peak was found caused by QW coupling to charge trapped at surface states of AlGaAs. These states can be caused by e.g. oxidation of Al on the surface. The exact explanation for the redshift still needs further studies.

### 4.4 TiO\(_2\) photodegradation

This chapter discusses the results of publication V. In that publication photodegradation of aqueous salisylic acid by TiO\(_2\) was studied. The main motivation for the study was to determine the efficiency of the ALD TiO\(_2\) for the photodegradation of organic substances. The use of salisylic acid is based on the fact that it is widely used in food industry and it can be found from the wastewaters. It may have possible effects on health and the environment.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Substrate</th>
<th>Temperature (°C)</th>
<th>Crystallinity</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)C100</td>
<td>Si</td>
<td>300</td>
<td>Anatase</td>
<td>~3.1</td>
</tr>
<tr>
<td>TiO(_2)C500</td>
<td>Si</td>
<td>300</td>
<td>Anatase</td>
<td>22.3</td>
</tr>
<tr>
<td>TiO(_2)C1000</td>
<td>Si</td>
<td>300</td>
<td>Anatase</td>
<td>46.1</td>
</tr>
<tr>
<td>TiO(_2)C2000</td>
<td>Si</td>
<td>300</td>
<td>Anatase</td>
<td>101.5</td>
</tr>
<tr>
<td>TiO(_2)T150</td>
<td>Glass</td>
<td>150</td>
<td>Amorphous</td>
<td>59.8</td>
</tr>
<tr>
<td>TiO(_2)T250</td>
<td>Glass</td>
<td>250</td>
<td>Anatase</td>
<td>48.2</td>
</tr>
<tr>
<td>TiO(_2)T300</td>
<td>Glass</td>
<td>300</td>
<td>Anatase</td>
<td>46.2</td>
</tr>
<tr>
<td>TiO(_2)T400</td>
<td>Glass</td>
<td>400</td>
<td>Anatase + Rutile</td>
<td>41.9</td>
</tr>
<tr>
<td>TiO(_2)T450</td>
<td>Glass</td>
<td>450</td>
<td>Anatase + Rutile</td>
<td>41.8</td>
</tr>
</tbody>
</table>

The TiO\(_2\) films were grown on two different substrate types, namely glass and silicon (100). Effects of both thickness and deposition temperature on the photocatalytical activity were studied. The sample names and
measured properties are listed in Table 4.2. The film thickness and mass densities were measured by X-ray reflectivity. The density of the films varied in the range of 3.8-3.9 g/cm$^2$. The crystal structure of the film was determined by X-ray diffraction. Commercial Pilkington Active$^{TM}$ TiO$_2$ coated glass was used as a reference in this study. The UV light was generated using low pressure mercury arc lamp. The intensity of the light was 0.2 mW/cm$^2$ emitting 85% of the radiation in the range of 250 - 260 nm.

![Figure 4.8](image) Salisylic acid degradation by TiO$_2$ films grown at different temperatures and Pilkington Active$^{TM}$ as a reference.

The photodegradation rate of SA is shown in Fig. 4.8. The photodegradation rate was clearly higher compared to the Pilkington reference. Even the amorphous TiO$_2$ had a higher photodegradation rate than the Pilkington reference. TiO$_2$ deposition temperature had a clear effect on the photodegradation of SA. The fastest photodegradation rate was found when the TiO$_2$ layer was deposited at 400 - 450 $^\circ$C. The crystallinity of the film was a mixture of anatase and rutile in that temperature range. According to Mills et.al [69] the anatase phase has the strongest photocatalytical activity which differs from results obtained in this work.

The film thickness had a clear influence on the photodegradation rate. Figure 4.9 shows the effect of the film thickness and substrate on the SA photodegradation. The substrate of the samples was silicon except in the sample GS where the TiO$_2$ had been grown on a glass substrate. The growth temperature was 300 $^\circ$C. No photodegradation effect was observed when the film was thickness was 3 nm. The photodegradation rate increased with the thickness from 22 to 46 nm. The photodegradation efficiency as the function of the film thickness saturated for the thickness
Figure 4.9. Effect of the TiO$_2$ film thickness and substrate material on the one hour salisyl acid degradation.

over 46 nm. When the TiO$_2$ layer was grown on glass the photodegradation rate was slightly lower. The proposed mechanism in the publication V was Na$^+$ ion diffusion in to the TiO$_2$ film from the glass causing minor losses for the photocatalytic activity.
In this work physical properties of plasma enhanced ALD grown aluminum nitride films were investigated. New method for \( \text{Yb}_2\text{O}_3 \) deposition using ALD was developed. Two novel GaAs surface passivation methods using ALD technique were developed. The photodegradation properties of ALD grown TiO\(_2\) were studied.

Aluminum nitride is wide band gap semiconductor material used in various applications. Atomic concentrations, crystal structure, density and optical properties play a strong role in the utilization of AlN. In this work the effect of each process parameter on the film properties was investigated. The deposition temperature had the most significant effect on the AlN growth process. Hydrogen concentration in AlN decreased when the deposition temperature was increased. The minimum deposition temperature was 150 °C. Hydrogen content was shown to correlate with the refractive index and mass density of the film. The films were optically transparent. The cut off wavelength was 300 nm.

Ytterbium doped fibers are the preferred gain media in high power laser sources. Earlier fiber soots have been doped using conventional modified chemical vapor deposition (MCVD) technique. ALD is a promising alternative for MCVD because of the excellent conformality. This may lead to more uniform Yb atom distribution in the optical fiber which may reduce the photodarkening of Yb doped laser fibers. The ALD temperature window for the \( \text{Yb}_2\text{O}_3 \) process was 300 - 350 °C. Lower than 1 % thickness variation was reached with an optimized process. The growth rate for the process was 0.18-0.20 Å/cycle. TOF-ERDA measurement indicated that the hydrogen and carbon impurity levels were 1.1 % and 0.7 % respectively. The refractive index was between 1.86 and 1.89 in the near infrared region of 800–1600 nm.

Gallium arsenide is a widely used semiconductor material. The devel-
opment of GaAs devices is partly limited by surface recombination and Fermi level pinning on the GaAs surface. In this work the surface passivation of near-surface InGaAs QWs by ALD grown TiN and PEALD grown AlN thin films was investigated. The low-temperature PL and TRPL measurements showed that both TiN and AlN passivation increased significantly the PL intensity and carrier lifetime of the NSQWs. Passivation layers also protected the GaAs substrate against oxidation in the long run.

TiO$_2$ is a photocatalytically active material which can be used for example in the water cleaning processes. The motivation to use ALD for the photocatalytic layer manufacturing comes from the fact that ALD film grows conformally in complicated 3D structures. ALD can also be used for manufacturing of multilayers or doped materials which may offer more possibilities to develop more effective photocatalytically active layers. In this work the crystal structure of the ALD grown TiO$_2$ had the strongest impact on the photocatalytic degradation of salisylic acid (SA). The TiO$_2$ deposition temperature had a strong effect on the crystal structure. The highest degradation rate of SA with TiO$_2$ films required both anatase and rutile phases. The film consisting only of the anatase phase was less effective and the amorphous film did not show any photocatalytical activity. The photoactivity increased up to the 50 nm film thickness but it was not improved by thicker films.


