SYNTHESIS AND OPTOELECTRONICAL CHARACTERIZATION OF BORON PHOSPHIDE

Egbert Schroten
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1. Depth profiles obtained by SIMS, Auger analysis, or RBS to characterize heteroepitaxial interfaces cannot be correctly interpreted unless the interface and its structure have been inspected with the use of a microscope.

2. Strain caused by lattice mismatch in heteroepitaxial films could prove to be a strong asset in microelectromechanical systems.


3. Integration of at least one electrical contact in the synthesis route of 3D semiconductor structures is of great benefit for successful implementation in devices.

4. To rule out the influence of the substrate on the film characteristics, Meaudre et al. should have performed a growth kinetics analysis, in order to establish the growth regime of the polymorphous films.


5. Authors presenting research on Vapour Liquid Solid synthesis should indicate the direction of the substrate surface normal during growth.


6. Electrophoretic image displays do not need a threshold voltage for passive matrix addressing.


7. If the aim of the penal system is to encourage convicts to repent, Lady Justice should discard her blindfold.

8. Science systematically rejects unique events, whereas they are highly significant in the lives of human beings. Man will do his utmost to remain unique. The application of natural science in its entirety to individuals by the humanities will therefore lead to inhumanity.

9. The individualization of our society and the move towards more business-like daycare centers, as well as the concept of the “family as cornerstone (i.e. island) in society”, reduce the number of human beings to whom children bond. This is a bad development in a world in which cultures are no longer separated in space, and is dangerous for a society in which tolerance and mutual respect are highly valued.

These propositions are considered defensible and as such have been approved by the supervisor, Prof. Dr. J. Schoonman.
Stellingen behorende bij het proefschrift

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1. Diepteprofielen die verkregen worden met behulp van SIMS, Auger analyse, of RBS om heteroepitaxiale overgangen te karakteriseren kunnen niet goed geïnterpreteerd worden als (de structuur van) de overgang niet zichtbaar is gemaakt met behulp van een dwarsdoorsnede.

2. Spanningen veroorzaakt door verschil in roosterconstante kunnen een sterke troef zijn voor microelektromechanische systemen.

3. De integratie van ten minste één elektrisch contact in de synthesesroute voor 3-dimensionale halfgeleiderstructuren is een groot voordeel voor succesvolle toepassing.

4. Om de invloed van het substraat op de eigenschappen van de film uit te sluiten, hadden Meaudre et al. een analyse moeten uitvoeren naar de groeikinetiek, om daarmee het regime van de polymorphe films te bepalen.

5. Auteurs die onderzoek publiceren op het gebied van Vapour Liquid Solid synthese, zouden de oriëntatie van het substraat gedurende de groei moeten vermelden.

6. Electroforetische displays hebben geen drempelspanning nodig voor passieve matrix adressering.

7. Als het strafrecht zich tot doel stelt schuldigen tot inkeer te laten komen, moet vrome Justitia haar blinddoek in de kast laten hangen.

8. In de wetenschap worden eenmalige gebeurtenissen systematisch verworpen, terwijl die bij uitstek de levensloop van mensen bepalen. Mensen zullen zich tot het uiterste inspannen om uniek te zijn. Het zal daarom tot onmenselijkheid leiden als menswetenschappen natuurwetenschappelijke methoden onverkort op individuen gaan toepassen.

9. De individualisering van onze maatschappij, de verzakelijke verging van de kinderopvang, maar ook het gezin als hoeksteen van (lees elland in) onze samenleving reduceren het aantal personen waarmee kinderen op vertrouwelijke basis omgaan. Dit is geen goede ontwikkeling voor een wereld waar culturen niet meer ruimtelijk gescheiden zijn, en voor een samenleving waarin tolerantie en wederzijds respect als hoogste deugden gezien worden.

Deze stellingen worden verdedigbaar geacht, en zijn als zodanig goedgekeurd door de promotor, Prof. Dr. J. Schoonman.
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ter verkrijging van de graad van doctor aan de Technische Universiteit Delft,
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voorzitter van het College voor Promoties,
in het openbaar te verdedigen op dinsdag 16 september 2003 om 15.30 uur

door Egbert SCHROTEN

natuurkundig ingenieur
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Dit proefschrift is goedgekeurd door de promotor:
Prof. dr. J. Schoonman.

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Physicists must speak about things, for things cannot speak for themselves.

Man does not allow any other fellow to express his own secret of existence.

_Eugen Rosenstock-Huessy_
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Synthesis and optoelectronic characterization of boron phosphide
Chapter 1

MOTIVATION AND OUTLINE
1.1 Introduction

One of the challenges of present society is the reduction of the waste that accompanies our prosperity. Waste products have a dramatic influence on our environment. Directly in the form of polluted rivers, air and soil, indirectly by penetrating the food cycle (e.g. dioxin). There is an increasing number of indications that mankind induces a climate change, causing an increase in natural disasters. Our pursuit, based on both our portrayal of mankind and on economic motives, aims at making the Western way of living attainable to a growing part of the world population.

Scaling up of the industrial processes in their present states will prove to be catastrophic, globalizing this standard of living [1]. However, diluting present prosperity is unacceptable and impossible. Instead, production methods will have to be changed dramatically; i.e. sustainability will be the main criterion, not cost effectiveness. Changes that fit developments seen today will have the highest probability of success.

Energy is one of the most important pillars of our economy. In this field, a wide range of activities is focused on more sustainable processes. Methods that do not produce waste during the course of generating power, using wind, tidal, or solar energy, are on the verge of competing with methods producing waste, like combustion and nuclear fission. The progressing electrification of both thinly populated areas and domestic appliances plays an important role in the development of competition in energy production methods. Photovoltaic power generation is most promising, due to its relative insensitivity to down-scaling.

The application of composites and coatings has proven to be an instrument to reduce waste. By combining different materials more efficient use can be made of raw materials. Replacement of traditional materials requires a thorough investigation of all alternatives. Data on the properties of a wide variety of materials is a prerequisite. For instance, the emergence of thin film solar cells have to be seen in this perspective. Despite the overwhelming advancement of silicon technology, other promising materials cannot be discarded to date. In particular, universities have the obligation to strike out upon new paths.

The investigations that are described in this thesis deal with the relatively unknown material boron phosphide. In our laboratory, it has its roots in the work of Goossens [2] and Kelder [3]. The synthesis, characterization, and application of this material are addressed. In order to put the contents of the various chapters into perspective, an introduction
of III-V hetero-epitaxy (the stacking of trivalent boron and pentavalent phosphorus atoms on a silicon crystal) is given. In addition, a short overview of liquid junction solar cells is presented.

1.2 III-V hetero-epitaxy

1.2.1 Structural aspects

Although placing considerable constraints on the success of growth of III-V semiconductors, the majority of the growth experiments has been done using silicon as substrate. The reason for this is the strong position of silicon technology. It is much more advanced than that of any other semiconductor-based technology, and is accompanied by a vast infrastructure consisting of highly sophisticated, clean, reproducible and relatively cheap production methods, as well as a thorough knowledge of its properties. If it is possible to synthesize a III-V semiconductor on a silicon wafer, implementation in this silicon technology is possible.

Epitaxy is the oriented growth of layers on single crystalline substrates. The arrangement of the atoms of the growing layer is superimposed by the structure of the host crystal. The better the intrinsic (bulk) crystalline structure of substrate material matches that of the material that is desired, the better the results. A strong indication of the possibility of epitaxial growth is the lattice mismatch, i.e. the relative difference in the size of the unit cell of both crystals. However similar the silicon (diamond) crystal resembles the III-V zincblende structure, a distinct difference has to be taken into account: the polarity of the surface. Both lattices can be regarded as two intertwined face centered cubes. For silicon, both sublattices consist of silicon atoms, and single atomic steps on the surface do not change the properties of the surface. For III-V crystals, one sublattice consists of group III atoms, the other of group V. In this structure, such a step does change the surface properties: one step on a (111) surface, would change the surface from all group III atoms to all group V atoms.

1.2.2 Electronic aspects

Most electronic devices are based on doped silicon, using the typical properties of p-n junctions. To be more precise, in one and the same semiconductor crystal, areas are doped according to specific patterns. Rectifying junctions and field effect transistors, for example, can be constructed. Junctions of different semiconductor materials provide an extra dimension to the possibilities of device design. Barriers can be introduced which only affect one of the
charge carrier types, thus creation of electron-hole pairs by light absorption can be localized. The modulation of bandgaps by so-called superlattices, a stack of thin layers of different bandgap materials, produces interesting possibilities to generate standing electron waves. The band edges of compound semiconductors can be shaped by the growth of gradual material transitions, such as In\textsubscript{x}Ga\textsubscript{1-x}As, in which x is varied in a spatial direction.

1.3 The liquid junction solar cell

Semiconductors are the base for the conversion of light into electrical energy. Photons that have an energy equal or larger than the bandgap of the semiconductor can be absorbed by electrons in the valence band. These electrons are excited into the conduction band, leaving a hole in the valence band. If these are separated before recombination takes place, an electrical potential difference is formed. This potential can be used, amongst others, to generate heat (light bulb), run electrical apparatus, charge batteries, emit light (LED), or prevent chemical reactions (corrosion protection).

For solar cells to obtain high conversion efficiencies, the absorbing layer has to be tuned to absorb as much direct sunlight as possible. The thickness of this layer must be chosen such, that recombination and ohmic losses are minimal, but that most of the incoming photons are captured to generate electron-hole pairs. Here, a great advantage of liquid junction cells emerges: using porous material, the mean path for electrons or holes to reach the junction (electrolyte) can be reduced without reducing the effective width of the absorbing layer.

Sensitization takes this idea even further: the light absorption and charge separation are now separated. Here, the absorption material can be optimized without the stringent demands on electrical properties. The use of organic dyes led to the design of the so-called Grätzel cell [4]. A nano-porous wide bandgap metal oxide semiconductor is covered with a mono-layer of dye molecules. An electrolyte containing a redox couple provides a Schottky contact. In the excited state after the absorption of a photon, the dye injects an electron into the semiconductor. The oxidized dye is reduced by species in the electrolyte. The electron travels through an external circuit, performing work, and finally reduces oxidizing species at the counter electrode.
1.4 Outline of this thesis

This thesis has three focal points: synthesis, characterization, and application of boron phosphide. Although these are intertwined, each subject is emphasized in two chapters each. Chapter two contains an overview of the different forms and methods of fabrication of boron phosphide. The fabrication method used in this study, i.e. Chemical Vapor Deposition (CVD), is described in detail. Chapter three presents an example of the influence of the synthesis method on the properties of the material obtained. It reports a high surface area of crystalline boron phosphide obtained by a surface treatment of the substrate.

The synthesis and characterization of thin films of cubic boron phosphide epitaxially grown on silicon is reported in chapter four. The following chapter zooms in on the determination of the fundamental band-to-band transition by electro-optical spectroscopic experiments.

The following two chapters are devoted to examples of applications of the results. Chapter six presents a thin-film solar cell based on the combination of different forms of boron phosphide. It is a nice example of the versatility of the CVD technique. Chapter seven reports the first results of an investigation to apply boron phosphide as a buffer layer for epitaxial growth of gallium nitride on silicon. The aim is to obtain a low defect heterostructure of GaN, a promising III-V semiconductor for optical applications, and silicon, the low cost semiconductor base material.

Finally, chapter eight presents an overview of the achievements and recommendations for further research.

1.5 Introductie

Een van de uitdagingen van de huidige samenleving is het terugdringen van het afval dat ontstaat als gevolg van onze welvaart. Er zijn nu al sterke aanwijzingen dat de afvalproducten die vrijkomen bij het in stand houden van de levensstandaard in rijke landen, grote gevolgen hebben voor bijvoorbeeld het klimaat. Ons streven (zowel vanuit ons mensbeeld als uit economische overwegingen) richt zich erop, die welvaart bereikbaar te maken voor een steeds groter deel van de wereldbevolking.

Opschaling van de huidige productiemethoden zal catastrofaal blijken bij het globaliseren van deze levensstandaard [1]. Echter, verdelen van de huidige welvaart is geen
optie. Daarom moeten de gebruikte methoden drastisch veranderd worden; duurzaamheid zal het belangrijkste criterium worden. De grootste kans van slagen hebben die veranderingen die aansluiten op de al bestaande ontwikkelingen.

Energie is één van de belangrijkste pijlers van onze economie. Er is dan ook al snel aandacht besteed aan een duurzame energievoorziening. Op het ogenblik kan het gebruik van onuitputbare energiebronnen als wind, getijdenwerking en zonlicht bijna concurren met methoden die tijdens de opwekking afval produceren, zoals verbranding en atoomsplitting. De voortschrijdende elektrificatie, van zowel huishoudelijke apparaten als van dun bevolkte gebieden, speelt een belangrijke rol in de concurrentie tussen methoden van energieopwekking. Fotovoltaïsche energieopwekking gooit hier hoge ogen, vooral vanwege de ongevoeligheid voor schaalverkleining.

Ook de toepassing van composieten en coatings is een goed antwoord gebleken op afvalreductie. Door het combineren van verschillende materialen kan in veel gevallen een veel efficiënter gebruik van grondstoffen bereikt worden. Eventuele vervanging van traditionele materialen vergt een grondig onderzoek van alternatieven, waarbij kennis van de eigenschappen van een grote diversiteit aan materialen noodzakelijk is. Ook de opkomst van dunne-film zonnecellen moet in dit licht gezien worden. Ondanks de overheersende siliciumtechnologie zijn er andere materialen die interessant genoeg lijken voor deze toepassing. Zeker universiteiten hebben de taak om het onderzoek te richten op weinig betreden terrein.


Hoofdstuk twee geeft een beschrijving van de bekende verschijningsvormen en van de fabricagemethodes voor dit materiaal. Dieper wordt ingegaan op de in het verdere onderzoek gebruikte synthesetechniek, de Chemische Vorming uit Damp (CVD). Een voorbeeld van de mogelijkheden die CVD biedt voor het vormgeven van een boriumfosfide structuur wordt gegeven in hoofdstuk drie.

In hoofdstuk vier wordt het onderzoek naar de eigenschappen van een dunne laag boriumfosfide op silicium beschreven. Het daarop volgende hoofdstuk is geheel gewijd aan de
resultaten van een elektro-optische analysetechniek, waarmee de fundamentele energietoestanden in kaart kunnen worden gebracht.

Hoofdstuk zes presenteert een dunne film zonnecel gebaseerd op een combinatie van verschillende vormen van boriumfosfide. Dit is een toepassing van de techniek beschreven in hoofdstuk drie. Het vormt een mooie illustratie van de kracht van dunne film technieken. In hoofdstuk zeven worden de eerste resultaten van een andere toepassingsmogelijkheid voor boriumfosfide gepresenteerd, namelijk als buffer tussen het alomgebruikte silicium en het veelbelovende materiaal galliumnitride.

Het laatste hoofdstuk bevat een samenvatting en suggesties voor verder onderzoek.
References


Chapter 2

BORON PHOSPHIDE: PROPERTIES AND SYNTHESIS

An overview of information on boron phosphide, found in literature, is presented. A limited amount of material properties of the different forms of boron phosphide has been published over the last century. Reviewing the different synthesis routes, chemical vapor deposition is found to be the most appropriate to produce material for this study. A set-up has been designed, and the precursor materials chosen. Because this deposition system has been used for all studies presented in this thesis, it is described in detail.
2.1 Properties of boron phosphide

2.1.1 Crystalline Boron Phosphide

Boron phosphide is an inorganic compound known in cubic, hexagonal and amorphous crystallographic form. This thesis will focus mainly on cubic BP, that is the most interesting form with respect to refractory and semiconducting properties. This material is built from two face-centred cubic sublattices, one consisting of boron and the other of phosphorus atoms. Although BP is member of the family of the III-V compounds, the resulting diamond-like structure is almost covalent, even more so than the IV-IV compound SiC. Boron phosphide has excellent physical and chemical properties for application as coating material and for use as active component in optical and electronic devices. It has a high hardness [1], and a high melting point and dissociation temperature (well above 1400 °C). Furthermore, the only known etchants for BP are fused alkalis at 400-500 °C [2].

Although the lattice parameter of silicon is 18% larger, boron phosphide can be grown epitaxially on silicon single crystals. This property is very important, because use can be made of the mature and relatively cost effective silicon technology. However, only a few papers have been published concerning the application of this material: as wide bandgap emitter transistor [3], optical window for silicon liquid-junction solar cells [4, 5], and as neutron detecting material, using the high neutron absorption cross section of $^{10}$B [6, 7].

In contrast to other members of the III-V family, the valence charge density in boron phosphide has two minima (instead of one) along the [111] axis, meaning that this material is considerably less polar [8]. However, the band diagrams calculated are similar to those of other III-V compounds [9]. Unfortunately, there is little experimental data available on the energy structure of boron phosphide. For thin polycrystalline films, Stone and Hill [10] have reported a direct bandgap of almost 6 eV and a shoulder in the transmission spectrum at 2 eV. Archer et al. [11] have determined the latter to be the fundamental, indirect band gap of 2.02 ±0.05 eV from experiments on small single BP crystals. The optical reflectance spectrum reported by Wang and co-workers [12] shows a weak maximum at 5.0 eV and a strong maximum at 6.9 eV tentatively attributed to transitions $\Gamma_{15} - \Gamma_{15}$ and $X_5 - X_1$ point of the Brillouin zone.

Theoretical data on the energy structure have been reported by several authors [13-17]. Values for an indirect gap of 1.2, 2.0, and 2.2 eV and for a direct gap of, respectively, 3.3, 2.0,
and 5.0 eV have been calculated. However, these values are known to be inaccurate with deviations of more than 100%. For instance, the local density approximation method, that produced the 1.2 eV indirect and 3.3 eV direct gaps, is known always to underestimate the true band-gap energies.

Publications addressing the properties of "hexagonal" boron phosphide are rare. The material is referred to as B₆P or B₁₅P₂. According to a careful study by Amberger [18], this material is derived from α-rhombic boron. On each corner of the cell, a B₁₂ icosahedron is situated. Aligned with the long axis of the cell, two atoms fill the inner space of the rhomboid. Both are bound to three icosahedra and to each other. These atoms can be a set of B and P, or two B atoms. Hexagonal BP is a hard material, and, contrary to the cubic form, shows a high electric resistivity.

2.1.2 Amorphous BP

The amorphous form of boron phosphide is a highly resistive semiconductor. In an extensive study of BP synthesized in the bromide CVD-system [19], Kelder has determined the B/P ratio never to be smaller than 3. Regarding literature, it is reasonable to use the name boron subphosphide, BₓP. Its optical bandgap lies in between 1.5 and 1.7 eV, depending on the stoichiometry. BₓP is under investigation for erosion protecting anti-reflection coatings in infra-red detecting systems [20], and represents a serious alternative for diamond-like-carbon.

Whereas subbandgap absorption in amorphous BₓP is very low, the material has a very high absorption coefficient above bandgap, comparable to that of amorphous silicon. Materials like these are suitable for thin film photovoltaic cells since less pure and expensive material is needed as active absorption and energy conversion layer. Although thin film cells require a relatively low conductivity, as compared to the thick crystalline cells, these amorphous semiconductors exhibit still too high resistivities. For amorphous silicon, that received most scientific attention, hydrogen incorporation proved a break-through [21]. Hydrogen binds dangling bonds, thus drastically increasing the mean free path of charge carriers. However, conductivities reported for BₓP films are too low [22,23] for solar cell application.
Chapter 2

2.2 Synthesis routes for BP

The high melting point (above 3000 °C) and the dissociation temperature of 1800 °C cause severe problems for synthesis of BP. Several routes have been reported so far, falling in two categories: growth from the melt and growth from vapor.

Crystallization from the melt, which is a desirable synthesis route for high-purity monocristalline semiconductors, requires high pressures to prevent decomposition. Kobayashi [24] and Ananthanarayanan [25] obtained small crystals of cubic BP by heating mixtures of boron and red phosphorus to temperatures between 1400 and 2400°C at pressures of 5 to 30 kBar. At more reasonable pressures, the melt can be obtained by a liquid-forming agent although this agent will contaminate the crystal [26, 27].

Growth of BP from vapor was first reported by Armington [28]. He produced crystals by a closed tube chemical transport method, using halogens as medium. The halogens carry boron and phosphorus from a hot to a relatively cold zone inside the tube: the reverse of the process in a halogen light bulb. The reproducibility of large crystals is difficult with this technique because randomly distributed nucleation sites are present on the fused silica tube. Special heat pre-treatment of the tubes is necessary to reduce the number of these sites, which yields a few, relatively large, crystals [29]. Growth of crystals of a few millimetres in diameter are obtained in 150 hours or more.

The problem of the nucleation sites can be solved by using specially prepared substrates in an open tube reactor. Instead of several randomly distributed sites, this substrate provides a footprint on which the crystal can grow. The vapor, a mixture of reactants, is forced to flow through the reaction tube and reacts at the substrate. The gaseous reaction products mix with the unreacted gas and leave the reactor. This technique, Chemical Vapor Deposition (CVD), is one of the most successful chemical transport methods. It is widely used in semiconductor and glass coating industry.

For the synthesis of monocristalline films of boron phosphide, several systems have been reported. Chu et al. [30] reported the growth of epitaxial layers on hexagonal SiC. A number of groups [29-34] used silicon single crystals as substrate, and reported successful epitaxial growth. All authors used hydride or halide precursors, the latter being reduced by hydrogen.
2.3 Chemical Vapor Deposition set-up

The synthesis route used in the present investigations is the reduction of the bromides $\text{BBr}_3$ and $\text{PBr}_3$ by hydrogen [35]. To obtain cubic boron phosphide, the overall reaction

$$\text{BBr}_3(g) + \text{PBr}_3(g) + 3\text{H}_2(g) \rightarrow \text{BP}(s) + 6\text{HBr}(g) \quad (2-1)$$

must be evoked. This is possible at temperatures above 860°C. The deposition parameters that determine the properties of the grown film are temperature (profile), pressure, precursor partial pressures, gas flow rate, and reactor dimensions.

Kelder [36] has reported an extensive study of the reaction mechanism of the gas mixture in a hot-wall system. He found that $\text{BHBr}_2$ is the dominating boron containing gas species that participates in the surface reaction. The phosphorus is supplied by $\text{PBr}_3$ at gas temperatures below 925°C, while at higher temperatures $\text{P}_2$ takes over. By studying the dependence of the growth rates on the reaction parameters, this transition can be found experimentally. The effect of the main parameters in this system, temperature and $\text{PBr}_3$/BBR$_3$ precursor ratio, is shown in Figure 2-1. The growth of boron phosphide takes place at temperatures between 860 and 1000 °C. The transition of the dominating phosphorus species taking part in the reaction (from $\text{PBr}_3$ to $\text{P}_2$) can be seen as a sharp change in the temperature/precursor-ratio slope of the BP-phase boundary.

The chemical vapour deposition set-up presented in Figure 2-2 has been used for all synthesis experiments in this study. The mixture of precursors and carrier gas is controlled by a gas distribution system. Here, the liquid precursors are evaporated into hydrogen in bubblers, and the concentration (partial pressure) is controlled by refluxing at a precise

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**Figure 2-1. CVD-diagram of the $\text{H}_2$-$\text{BBBr}_3$-$\text{PBr}_3$-gas system [36]. The boundary indicated by # is caused by a depletion of the $\text{PBr}_3$ in favor of $\text{P}_2$ and $\text{HBr}$. The boundaries marked * and ** are due to the depletion of $\text{P}_2$. The different boundaries found for $\text{SiO}_2$ (*) and $\text{Al}_2\text{O}_3$ (**) substrates are attributed to differences in nucleation behavior.**
temperature. The precursor gasses are led through heated lines, diluted and mixed prior to introduction into the reaction chamber. This chamber is a vertical quartz reactor tube having water cooled walls. Inside the tube, a graphite susceptor is positioned on top of a alumina pedestal. The graphite is heated by an induction coil, and acts as the substrate holder. Exhaust gases are led through a bubbler filled with an aqueous 2 molar NaOH solution to neutralize the bromide. A vacuum pump is used to remove oxygen prior to deposition; the reactor is repeatedly pumped and flushed with hydrogen.

Figure 2-2. Cold wall, induction heated Chemical Vapor Deposition set-up, used for the synthesis of boron phosphide.

2.4 Synthesis of BP

2.4.1 Epitaxial growth on silicon

For the synthesis of epitaxial films of BP on Si, several pieces of Si wafer (both n- and p-type, slightly off-oriented (100)) have been used. They are thoroughly cleaned in acetone, oxidized in 98% HNO₃, quickly etched in 10% HF for 30 seconds, and placed in the reactor. Between each step in the cleaning procedure, the silicon is rinsed with water. Particular care has been taken to remove all phosphorus in the reactor. This contamination is abundant on the reactor wall and alumina pedestal after a deposition. The phosphorus on the reactor tube is dissolved in acetone, after which the tube is cleaned in ethanol and distilled water. On a regular base, the alumina pedestal is heated in air for 10 hours at 600 °C. Inside the reactor, the Si substrates are heated to 950 °C in a small hydrogen flow for ten minutes to obtain a reconstructed H-
terminated surface. The reaction gas mixture is a hydrogen gas flow of 1750 ml/min. with partial pressures of 3.0 and 0.15 Torr for PBr<sub>3</sub> and BBr<sub>3</sub>, respectively. The introduction of the reaction gases is started by increasing the hydrogen flow, followed by addition of the phosphorus precursor. Prior to the introduction of the boron precursor a delay of 5 seconds is maintained to prevent the formation of a boron rich B<sub>x</sub>P compound. Typical growth time is 20 minutes, in which a film of approximately 200 nm is deposited. In a number of depositions, a small flow of silane/argon mixture (2 % SiH<sub>4</sub> in Ar, Electronic Grade, Air Products) has been added as doping gas. Temperatures are measured using an optical pyrometer, accuracy of the measurement is estimated to be 3 °C, whereas the temperature at centre of the susceptor surface is found to be less than 5 °C lower than at the susceptor edge.

2.4.2 Amorphous B<sub>x</sub>P

To obtain the amorphous phase, the reaction set-up does not need any change. An increase in partial pressure of the boron precursor shifts the deposition condition from the crystalline into the amorphous phase. This is a convenient way of supplying an amorphous coating onto crystalline BP (see Chapter 6).

For optical characterization of amorphous B<sub>x</sub>P, the homogeneity is very important. Local or temporal differences in temperature or partial gas pressures will result in compositional fluctuations within the deposit. These fluctuations cause differences in optical properties. Therefore, a hot-wall reactor is used for these experiments: the double walled quartz reaction tube is replaced by a single walled tube. The RF induction coil is replaced by a small tube oven. A graphite disc on an alumina tube supports the substrate. Inside the alumina tube, a thermocouple is inserted into the graphite disc, to record the temperature of the graphite. Protected by a quartz cover, the metal thermocouple is not exposed to the reaction gas. The temperature gradient inside the tube oven is small, as determined by inserting a second thermocouple from the top of the tube. At atmospheric pressures, using hydrogen as a carrier gas, the temperature difference between the graphite and the growing layer is less than 1 °C.

2.5 Summary and Conclusions

In this chapter, an overview of the available data on boron phosphide is given. The material properties indicate that this III-V semiconductor material deserves more scientific interest. Fundamental semiconductor theory can extract data that are not very similar to the III-V
compounds that have been studied more intensely. For applied semiconductor material science boron phosphide is a material with outstanding material properties. Its elements are not alien to most semiconductor synthesis systems (either as a dopant or as a constituent of another compound).

Although several synthesis routes are known, chemical vapour deposition is the best candidate to provide pure material samples that are relatively easy to handle. In addition, this route is compatible with semiconductor technology where thin films form the basis of most devices.

Adjusting synthesis parameters temperature and partial gas pressures provides the means to produce thin layers of material exhibiting specific properties. Our particular set-up had three regimes corresponding to epitaxial, polycrystalline, and amorphous material.

Given the rudimentary status of data on boron phosphide, we decided that the most effective modus operandi was not to restrict this study to one single application. We selected several topics to obtain new data and to demonstrate the opportunities this material provides.
References

21 Hydrogen incorporation in a-silicon.
References continued

Chapter 3 *

SYNTHESIS OF NANOMETER-SCALE BORON PHOSPHIDE WHISKERS BY VAPOR-LIQUID-SOLID CHEMICAL VAPOR DEPOSITION

Densely packed layers of boron phosphide whiskers have been grown on quartz, tungsten, and graphite substrates by chemical vapor deposition. Nickel and silver acted as liquid forming agents in a vapor-liquid-solid growth mechanism. The formed whiskers have diameters typically between 10 and 5000 nanometers, depending on the substrate material, the seeding metal, and the synthesis temperature. The length of the whiskers can be as large as 0.1 millimeter. High-resolution transmission electron microscopy imaging revealed that the whiskers are single crystalline with a large number of twin faces.

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Synthesis and optoelectronical characterization of boron phosphide
Chapter 3

3.1 Introduction

Boron phosphide (BP) is a III-V semiconductor with an indirect band gap of 2.0 eV and a zinc-blende crystal structure [1]. As was pointed out by Kelder et al., this rather unknown semiconductor has the mechanical and chemical properties of refractory materials, such as a Vickers hardness similar to that of TiN. BP was investigated as a protecting optical window for silicon in photo-electrochemical cells [3]. In that study, epitaxial BP(100) films were deposited by CVD on both n- and p-type Si(100) substrates. It was shown that the conduction bands of Si and BP match quite well, whereas a potential barrier of 0.9 Volt is present between the valence bands of these two semiconductors.

The growth mechanism of whiskers has been a topic of intensive research for many years. To date, it is widely accepted that a vapor-liquid-solid (VLS) mechanism, as proposed by Wagner and Ellis in 1964 [4], is most successful in explaining the highly anisotropic growth of these crystals. In contrast to growth rates in conventional heterogeneous vapor-solid film syntheses, the unidirectional high growth rate is caused by effective supply of reactants to specific nucleation sites. Necessary for this mechanism is a liquid forming agent, such as metallic impurities, on the substrate surface. At the deposition temperature (around 900 °C for BP) the precursors dissociate and dissolve into the molten Ni or Ag seeds. When saturation is reached, crystallization of the product starts at the liquid-solid interface and after a while the formed crystallite pushes the seed metal droplet away from the substrate. Continuation of this process results in whisker formation.

Here we report on the study of thin BP films with a large physical surface area. These layers of whiskers have been synthesized on different substrates. Nano-structured semiconductor thin films have recently aroused scientific and technological interest because of the discovery of luminescent porous Si [5], and the remarkable success of the Grätzel-type liquid junction photovoltaic solar cells [6]. High surface area electrodes of the chemically stable semiconductor BP may also be applicable as gas sensor, in photocatalysis, and for energy conversion purposes. While BP whiskers can easily be obtained by CVD using VLS [7], little has been reported on relations between process conditions and whisker morphology. We investigated the influence of different seed metals and substrate materials, as well as the deposition parameters on the VLS-growth characteristics of BP whiskers.
3.2 Experimental Aspects

Boron phosphide whiskers were synthesized in a vertical cold-wall CVD-reactor (inner diameter 36 mm) using inductive susceptor heating. The precursors, BBr₃ (Alfa el. grade 99.99 %) and PBr₃ (Merck Suprapur > 99 %), were diluted in H₂ (99.999 %, Pd-purified and dried) carrier gas and reacted on the substrate, which was heated to temperatures ranging from 850 to 1000 °C. Partial pressures were varied in the range of 0.2 to 0.5 Torr for BBr₃ and 2.0 to 5.0 Torr for PBr₃, flow rates ranged between 0.8 and 1.5 l/min. The substrate materials investigated were quartz, tungsten, and graphite, which were dipcoated in a 0.02 M solution of nickel or silver acetate (Baker anal. grade). In order to remove all oxygen and carbon contamination, the substrate was reduced in H₂ at 900 °C prior to the deposition. Two or three substrates, of typically 10x10 mm, were coated simultaneously in one experiment.

For high-resolution transmission electron microscopy (TEM) analysis small graphite substrates were used which could be placed into the microscope. Since the constituents boron and phosphorus both have low electron-scattering cross sections, the whiskers did not need further preparation.

3.3 Results and Discussion

During the CVD-VLS process, layers of randomly oriented whiskers are formed. The diameter of the whiskers strongly depends on the substrate material, the seeding solution, the deposition temperature, and the deposition time. Typical axial growth rates are 0.5 μm/min, whereas radial growth rates are at least two orders of magnitude less. An increase of the reactant partial pressures or flows results in higher growth rates, but does not significantly change the shape.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Seed</th>
<th>Temperature</th>
<th>Typical diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>Ni</td>
<td>&lt; 930 °C</td>
<td>0.01 - 0.1 μm</td>
</tr>
<tr>
<td>Graphite</td>
<td>Ni</td>
<td>&gt; 940 °C</td>
<td>1 - 5 μm</td>
</tr>
<tr>
<td>Graphite</td>
<td>Ag</td>
<td>880-1000 °C</td>
<td>1 - 10 μm</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Ni, Ag</td>
<td>930 °C</td>
<td>1 - 5 μm</td>
</tr>
<tr>
<td>Quartz</td>
<td>Ni</td>
<td>880-1000 °C</td>
<td>0.1 - 5 μm</td>
</tr>
</tbody>
</table>

Table 3-I Summary of BP whisker formation on C, W, and quartz substrates. The gas-flow rates in the reactor were equal; typical deposition time was 20 minutes.
of the whiskers. Table 3-1 contains a summary of the different combinations of the substrate materials and seeding solutions that were investigated, and the typical whisker diameters obtained.

Scanning electron micrographs of the whiskers with large diameters show distinct crystal faces. At low deposition temperatures, the whiskers have hexagonal morphology (see Figure 3-1a), whereas at high temperatures the crystals are triangular (Figure 3-1b). Near the tip of the high-temperature grown whiskers, three additional faces appear, again showing the hexagonal form. The hexagonal shape in a zinc-blende crystal strongly suggests that preferred growth occurs along the (111) direction. At high growth temperatures, the side faces of the whiskers are smooth, whereas at lower temperatures, 'stepped' surfaces and branching appear (Figure 3-1c). High-resolution TEM-pictures (Figure 3-2) reveal the crystal structure of the small-diameter whiskers. Micrographs reveal crystals which contain a high density of twin planes, spaced approximately 10 to 20 nm apart. Surprisingly, EDX element analysis on the whisker tips did not reveal any traces of nickel, while X-rays attributed to nickel were found when the electron beam grazed the graphite surface.

Figure 3-1. SEM-pictures of large-diameter whiskers grown on graphite activated with NiAc₂ at 980°C (a), and 950°C (b). Stepped side faces grown at 890°C on graphite dipcoated in AgAc (c).
Nickel or silver on the substrate surface is responsible for the growth of whiskers, because it is found that substrates which had not been treated with NiAc$_2$ or AgAc are covered with a dense layer of polycrystalline BP rather than whiskers. The nature of the substrate plays an important role in the whisker diameter. It influences the size of the seed, and thus the initial whisker diameter. For graphite substrates dipped into NiAc$_2$, the deposition temperature dependence of the whisker diameters shows two regimes, one of small (tens to hundreds of nanometers) and one of large (1-5 microns) diameter whiskers. Since no such behavior is observed in the Ag-catalyzed depositions, the two types of whiskers are related to the specific interactions of nickel with graphite. The Ni catalyst promotes hydrocarbon formation which leads to etch pits on the substrate [8], preventing the sintering of Ni into larger seeds. The large-diameter regime must be caused by an increase in the seed size. A strong increase in wetting of the substrate, reported by Baker [9] for temperatures above 1000°C in low pressure environment, could also operate at slightly lower temperatures in our system.

For tungsten and quartz substrates, an approximate linear relationship between the temperature and the diameter is found. This behavior can be explained by the size of the droplet/solid contact area which depends on the surface tension of the droplet material. Higher temperatures reduce this tension, and the droplets flatten. While initially the whisker diameter is determined by the size of the droplet, subsequent radial growth takes place by a conventional heterogeneous vapor solid reaction mechanism which, however, is much slower than the VLS growth. Thickening of the whiskers during growth occurs only to a very limited extent.

The stepped structure of the side faces of whiskers formed at low growth temperatures can be explained as follows. A periodic change in the surface tension of the liquid, due to variations in growth temperature, is expected for exothermic reactions. The droplets heat up
and flatten, resulting in a larger surface, and hence an increased heat loss with subsequent temperature drop. This does not necessarily converge to a stable temperature due to the changes in solubility of the species in the liquid which also influences the surface tension. An alternative explanation of the side-face morphology is the restricted surface mobility of adsorbed gas species to the side faces since higher mobilities at elevated temperatures enable the crystal to lose its surface roughness.

3.4 Conclusions
Whiskers of boron phosphide can be synthesized by a VLS-mechanism in which nickel or silver acts as a liquid forming agent. The whiskers have typical lengths of hundreds of microns and diameters that depend linearly on temperature for quartz and tungsten substrates. For carbon substrates with Ni seeds at growth temperatures below 930°C, the diameter of the whiskers is restricted to several tens of nanometers. The whiskers are of highly twinned single crystallinity, with a preferred growth along the (111) direction.

3.5 Acknowledgements
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References


Chapter 4

INVESTIGATION OF SI/BP HETEROSTRUCTURES

This paper presents the results of an investigation into the properties of the boron phosphide / silicon heterojunction. Epitaxial films of this III-V compound have been deposited on silicon (100) substrates by chemical vapor deposition, employing the BBr$_3$-PBr$_3$-H$_2$ system. The large lattice mismatch (17%) is accommodated by interstitial planes, that originate in the first few atomic layers of the boron phosphide. We obtained three types of structures: n-BP on both n- and p-type Si, and p-BP on n-Si by adding a small flow of SiH$_4$ to the gas mixture. Capacitance-voltage analysis shows an effective donor density of 4.2×10$^{18}$ cm$^{-3}$ for n-BP and an effective acceptor density of 6×10$^{19}$ cm$^{-3}$ for the Si-doped films on n-Si. Analysis of open circuit voltages generated by illumination suggests that the band alignment can be modeled using the Anderson approach. However, surface-photovoltage measurements indicate that the band line-up is accompanied by Fermi level pinning close to midgap position.
Synthesis and optoelectronical characterization of boron phosphide
4.1 Introduction

Over the last two decades, much research effort has been put into the growth and characterization of compound semiconductors as an alternative for silicon in several integrated circuit applications. However, the possibility to integrate these compound materials with silicon into heterostructures is still considered to be vital for technological interest in these materials. In addition, the heterojunction in itself widens the possibilities for devices due to the formation of "charge carrier selective" barriers and optical windows [1]. Especially in optical applications, such as lasers and detectors, heterojunctions are widely applied at present. The electrical behavior of these structures is largely determined by the distribution of the difference in bandgap over both bands, and the formation of interface states inside the gap. A collection of important papers in this field has been republished by Margaritondo [2]. The study of particular heterostructures is greatly helped if experimental data from two or more of the four possible heterojunction types (p-n and n-p anisotype, and n-n and p-p isotype) are combined.

Most effort in semiconductor material research has been focused on compounds that are compatible with silicon or GaAs. In principle, this requires a matched lattice parameter. However, large mismatches do not automatically lead to incompatible situations. In spite of the silicon lattice parameter being 20% larger, boron phosphide (BP) can be grown epitaxially on Si (100) and (111) surfaces [3-5]. Early reports suggest that an amorphous buffer layer acts as an intermediate between the two different lattices. However, more recently, high resolution TEM studies show the mismatch is accommodated by interstitial planes and twinning [6].

Boron phosphide is a relatively unknown member of the III-V semiconductor family. This 2.0 eV indirect bandgap material shows excellent hardness and chemical stability [7], and is investigated for application in wide bandgap emitter transistors [8], as protective optical window in IR detection [9] and for liquid junction solar cells [10-12]. A review of the material has been reported by Kumashiro [13]. Still, there is scarce data on the electrical properties of this material [14]. Like in all compound semiconductors, a deviation of stoichiometry can lead to high concentrations of donors or acceptors. Furthermore, diffusion and substitutional doping by silicon from the substrate can result in high doping levels at least close to the interface. Silicon is an amphoteric dopant, and although most early papers agree on high Si
concentrations found in the BP films [15], no direct relation to the conduction type has been established.

In this paper, we present the status of our investigations into the properties of the Si/BP heterojunction. To clarify the atomic arrangement across the Si/BP interface, we have studied these structures using high-resolution transmission electron microscopy. The interface structure is related to the conditions during first stages of growth. We studied the effect of silane added to the reactant mixture, which influences both the structure and the electrical behavior of the grown film. The heterostructures obtained have been subject to optical and electrical analysis in order to gain insight into the properties of the BP film. Finally, this information is used to shed light on the electronic structure of the junction.

4.2 Electronic structure of heterojunctions

One of the most important issues in understanding the electronic behavior of semiconductor heterojunctions is the distribution of the discontinuity of the electronic bands caused by the difference in bandgap. This problem was first addressed by Anderson [16], who treated the electronic structure of a perfect heterojunction. He constructed band diagrams for heterojunction using the vacuum level as external reference. The conduction band edge discontinuity is equal to the difference in electron affinity of the semiconductors. Electron affinity is the negative of the electron-gain enthalpy [17]. For a semiconductor, the electron affinity is the energy needed to extract an electron from the bottom of the conduction band and place it outside the material. In contrast to the work function, this parameter is not strongly dependent on the doping level of the material. However, the electron affinity of BP is not known. The concept of electronegativity can be used to obtain a quantitative scale for the band alignment. Electronegativity is the power of an atom to attract electrons in the molecule the atom is part of.

Table 4-1 Electronegativities of the atoms involved in the heterojunction according to refs. 18, 19, and 20. For Si and the BP compound, the conversion to a relative energy scale is shown.

<table>
<thead>
<tr>
<th></th>
<th>Pauling</th>
<th>Sargent-Welch</th>
<th>Miedema</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.90</td>
<td>1.98</td>
<td>3.54 eV</td>
</tr>
<tr>
<td>B</td>
<td>2.04</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>2.19</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>BP</td>
<td>2.11</td>
<td>2.00</td>
<td>3.58 eV</td>
</tr>
</tbody>
</table>
There are different approaches to construct a set of electronegativities, depending on the nature of the atomic bonds. In Table 4-I, the values applicable in this study are tabulated, following Pauling [18] (revised by Sargent-Welch [19]) and Miedema [20]. The average electronegativity of BP is taken as the geometric mean of those of its constituents. While the Pauling set is derived from data involving molecules, the latter is based on thermodynamic data of metals and alloys. Since the Pauling values for Si, B, as well as P lie in the range typical of metals and metalloids, the Miedema-set can be used.

![Diagram](image)

Figure 4-1. *Theoretical band line-up of ideal BP/Si heterojunctions according to the Anderson model. All four possible junction types are shown: two isotype junctions (top), two anisotype junctions (bottom).*

Figure 4-2. *Theoretical band line-ups of the four types of Si/BP junctions, assuming Fermi level pinning at midgap position: isotype junctions (top), anisotype junctions (bottom).*

To obtain quantitative data for the determination of the band off-sets, the values of Table 4-I have been converted to the energy scale. Relative values can be obtained by using the conversion coefficients of 1.79 eV (Pauling) and 0.93 eV (Miedema) [21], predicting a very small discontinuity of -0.04 eV in the conduction band going from BP to Si.

To construct the band diagram of the junction in equilibrium, the Fermi levels must be aligned. The difference in work function in the bulk of the materials generates a potential drop over the interface, causing band bending. If the interface states are neglected, the distribution of the total bending can be derived from
\[
\frac{B_{Si}}{B_{BP}} = \frac{N_{BP} \cdot \varepsilon_{BP}}{N_{Si} \cdot \varepsilon_{Si}} \tag{4-1}
\]

where \( B \) is the band bending, \( N \) the doping density, and \( \varepsilon \) the dielectric constant. Assuming all materials to have the same level of doping, the band diagrams of the four possible BP/Si junctions, as derived from the Anderson model, can be constructed (Figure 4-1). This model has many successors, either exploring possible energy scales [22], or introducing gap states caused by the penetration of complex wave functions into the other material [23]. These are still theoretical treatments of ideal junctions. The modeling of real heterojunctions and the design and interpretation of experiments is a big challenge.

Various methods to gather experimental data have been subject to strong debate on the interpretation; the problem lays bare the fundamentals of semiconductor physics. Due to this lack of experimental backing, modeling of heterostructures is still highly speculative, except for the widely studied Si/Ge junction and the Al\(_x\)Ga\(_{1-x}\)As compounds. However, for a comprehensive knowledge of semiconductor heterostructures, data on a variety of semiconductor materials is needed.

The most important barrier to obtain experimental data on electrical behavior of heterojunctions is the occurrence of interface states caused by mechanical stress. This is mainly due to a difference in thermal expansion coefficients of the two materials. Fabrication of heterostructures usually takes place at high temperatures, and cooling down to room temperature leads to interface states that have a strong effect on the electronic behavior of the structure. For those junctions in which stress and defects can be expected to play a major role, the Anderson approach is not expected to satisfy. Following Wieder [24] and Spicer [25], the effect of interface states on the alignment of the band edges can be estimated. If the defect density exceeds \(10^{14} \text{ cm}^{-2}\), the Fermi level will be pinned by the defect states. The position of the Fermi level at the interface can be determined by imposing charge neutrality.

For the BP/Si heterojunction, the interface state density will be high due to the difference in thermal expansion, and the lattice mismatch. We expect these effects to be independent on conductivity type of the semiconductors involved. If we assume the states originating from stress and mismatch to be distributed symmetrically over the gap, the Fermi level will be pinned close to midgap position. Alternative band diagrams of the four types of Si/BP heterostructures can be constructed (Figure 4-2). For the anisotype structures, the correction to the Anderson model (Figure 4-1) does not qualitatively change the band bending. For the isotype junctions, however, the direction of the band bending in silicon at the
interface is reversed. This provides a possibility to link these models to the current-voltage behavior of real structures.

4.3 Experimental aspects

4.3.1 Synthesis of Si/BP junctions

Samples have been prepared in an induction heated, cold wall chemical vapor deposition set-up (Figure 4-3), using the precursors BBr₃ and PBr₃ diluted in H₂. Kelder et. al. [26] reported an intensive study on the surface thermodynamics governing the growth mechanisms in this system. Reaction takes place under atmospheric pressure at temperatures around 900°C. The pieces of Si wafer (both n- and p-type, slightly off-oriented (100)) are thoroughly cleaned in acetone, oxidized in 98% HNO₃, quickly etched in 10% HF for 30 seconds, and placed on top of a graphite susceptor. Between each step in the cleaning procedure, the silicon is rinsed with water. Particular care has been taken to remove all phosphorus in the reactor. This contamination is abundant on the reactor wall and alumina pedestal after a deposition. The phosphorus on the reactor tube is dissolved in acetone, after which the tube is cleaned in ethanol and distilled water. The alumina pedestal is heated in air for 10 hours at 600 °C. For

![Figure 4-3. Schematic drawing of the deposition set-up for epitaxial growth of BP on Si(100) substrates.](image)

comparison, a number of depositions without this phosphorus cleaning procedure has been carried out. Inside the reactor, the Si substrates are heated to 950 °C in a small hydrogen flow for ten minutes to obtain a reconstructed H-terminated surface. The reaction gas mixture is a hydrogen gas flow of 1750 ml/min. with partial pressures of 3.0 and 0.15 Torr for PBr₃ and
Synthesis and optoelectronical characterization of boron phosphide

BB\(_3\), respectively. The introduction of the reaction gases is started by increasing the hydrogen flow, followed by addition of the phosphorus precursor. Prior to the introduction of the boron precursor a delay of 5 seconds is maintained to prevent the formation of a boron rich B\(_2\)P compound. Typical growth time is 20 minutes, in which a film of approximately 200 nm is deposited. In a number of depositions, a small flow of silane/argon mixture (2 % Si\(_\text{II}\) in Ar, Electronic Grade, Air Products) has been added as doping gas. Temperatures are measured using an optical pyrometer, accuracy of the measurement is estimated to be 3°C, whereas the temperature at center of the susceptor surface is found to be less than 5°C lower than at the susceptor edge.

4.3.2 Characterization

After synthesis, the structural properties of the samples have been examined. For determination of layer thickness, optical reflection spectra have been recorded (Varian UV-VIS-NIR photospectrometer). The crystallographic orientations are probed by X-ray diffraction using a Philips PW1840 powder diffractometer. The sample is positioned in such a way, that the Si(400) reflection falls into the detector. It must be noted that this method can introduce shifts in both amplitude and peak position if the samples are slightly off-oriented. In that case, the signal originates from the shoulder of the diffraction peaks, and the form of these peaks depends strongly on lattice distortions. During the scan, a small interval around the strong Si(400) reflection is left out to prevent saturation of the detector. The BP films are considered not to be epitaxial if the BP(200) and BP(400) are absent, as well as samples that show the BP(111) reflection. The epitaxial samples have been prepared for high-resolution transmission electron microscopy. Micrographs and selected area (electron) diffraction patterns have been obtained in a Philips CM-30-UT/FEG microscope.

For electrical characterization, the structures must be prepared in order to eliminate the possible electronic short cuts caused by the growth of BP or diffusion of boron or phosphorus at the sides of the silicon substrates. The diffusion depth of these atoms after 30 minutes at 1000 °C is several tenths of a micrometer. At each of the four sides of the samples, and at the Si back-side, approximately one micrometer of material has been removed by polishing.

The majority charge carrier type of the boron phosphide has been identified by determining the direction of the thermoelectric power, induced by applying a temperature difference of 100 °C over two or three millimeters. Dopant concentrations in the grown films have been determined by electrical modulation techniques in a three electrode electrochemical cell. After thorough cleaning in acetone, ethanol and water, the sample is mounted on a PVC
disc with a hole of 2 mm diameter. Through this hole, the BP-side of the samples is brought in
(rectifying) contact with an indifferent aqueous electrolyte (0.1 M NaOH). An
electrochemical interface (Solartron Model 1286), connected to a frequency response analyzer
(Solartron Model 1255) is used to gather data on the behavior of the electrode in response to
small ac signals at different polarizations.

To obtain current-voltage characteristics of the heterostructures, ohmic contacts of In-
Ga have been applied at the Si back side and the top of the BP film. The ohmic nature of the
In-Ga on BP is confirmed by I-V analysis of Al/BP/InGa and Au/BP/InGa. For this Al and Au
dots have been evaporated on several samples. Current-voltage data of the BP/Si heterostructures are obtained both in dark and in white light conditions. Illumination of the
BP film is provided by a halogen light source through glass fibre optics (Oriel cold light), care
has been taken to minimize the InGa wetted area of the BP to reduce the blocking of the light.

Finally, the energy band structure of the heterojunction has been probed using surface-
photovoltage analysis [27]. The free silicon surface of the three different structures (two
isotype and one anisotype junction) has been provided with an eutectic In-Ga contact.
Surface-photovoltage has been determined using a Kelvin probe, of which the electrode
consisted of a circular golden grid of 2 mm diameter. By illumination through this grid, the
effect of creation of photocarriers is studied. An optical system of a 50 W halogen light
source, a water filter, and a lens have been used to focus the light on the BP film and silicon
substrate beneath. With the aid of neutral density filters and a 795 nm long pass filter, an
illumination sequence is performed, during which the surface voltage is recorded: starting in
the dark, followed by a period of red light illumination, a period of white light, and finally a
period dark. The red light is sub-bandgap for the bulk of the BP layer.

4.4 Results

4.4.1 Structural characterization of Si/BP junctions

The free surface of the BP films of 200-300 nm thickness is shiny and colourless, showing
roughness of only a few nanometers. Sometimes, coloured interference rings are clearly
visible at the edges. Surfaces of films with thicknesses over 1 μm tend to roughen
considerably, showing a grey, scattering appearance.

The first indication on the crystallinity of the grown BP films has been obtained by X-ray
diffraction. Figure 4-4 shows a typical diffraction spectrum of an undoped epitaxial boron
phosphide film. Peaks are present at 38° and 82° 2-theta, corresponding to the (200) and (400)
Figure 4-4. *X-ray diffraction spectrum of the BP/Si sample obtained in a powder X-ray diffractometer.* The sample orientation has been chosen to obtain the Si(400) reflection. The BP(200) superreflection and BP(400) are clearly visible, the strong Si(400) reflection is suppressed. The reflection at 62° 2θ is caused by the BP(211) plane, which existence is caused by twinning.

reflections. An additional peak of varying intensity is found at 62°. If the ratio of the boron to phosphorus precursor partial pressure is higher than 0.5, no epitaxial growth is observed. Instead, a boron rich amorphous phase is formed. This maximum for the precursor ratio is valid for a deposition temperature of 930 °C, and decreases slightly upon changing this temperature. The minimum substrate temperature at which BP films are obtained is found to be 860 °C.

Addition of SiH₄ to the source gas mixture influences the epitaxial growth. Mixtures with partial SiH₄ pressure exceeding 0.062 Torr lead to the growth of amorphous films. However, although n- and p-type substrates have been used simultaneously, the maximum SiH₄ partial pressure to obtain epitaxial growth on p-type silicon is found to be even lower, i.e. 0.04 Torr.
Figure 4-5. Transmission Electron Micrograph showing a smooth CVD-grown epitaxial film of BP on Si(100). Fringes at both sides of the interface reveal considerable stress.

The interference patterns in the optical reflection spectra can be used to determine the thickness of the BP films. Assuming a constant index of refraction of 3.1 [1], a growth rate of 10 nm/min. is found for a deposition temperature of 900 °C. The samples that have been analyzed in the TEM confirm the thickness found by this approach within a few percent. A cross section of a 180 nm film of epitaxial BP on Si(100) is shown in Figure 4-5. The surface is smooth, and the BP/Si interface is clearly visible.
Figure 4-6. High-resolution micrograph of the Si/BP interface. Following the (111) planes, indicated by the arrow, the additional atomic planes that accommodate the lattice mismatch between the BP and Si crystal are clearly visible.

On both sides of the interface, fringes in the electron image are present. Zooming in at the boron phosphide/silicon interface shows the stacking of the atomic planes at both sides of the junction (Figure 4-6). Following the {111} planes across the interface (indicated by the arrow), a large number of interstitial planes appears at the BP side of the junction. A high density of twin boundaries shows as dark lines in the electron image, extending into the BP film. The distance of the twin faces varies down to several Ångstroms. Selective area diffraction patterns (SADP) show four twin types, obtained by a 60° rotation around <111>. In Figure 4-7 corresponding SADP's are shown. Most of the twin boundaries are annihilated within the first 100 nm of the epilayer.
Figure 4-7. Electron diffraction patterns of epitaxial film of BP grown on Si: (a) a (100) oriented crystallite, (b) and (c) show twinning.

The effect of phosphorus on the interface, if present in the reactor prior to growth, can be seen in Figure 4-8. This cross-sectional TEM graph shows the junction grown with a delay of 120 seconds between the introduction of the phosphorus and boron precursors. The BP/Si interface is dramatically roughened, which is best seen in the inserted dark field graph. This

Figure 4-8. High-resolution micrograph of the Si/BP interface grown in a reactor with phosphorus present in the alumina susceptor pedestal. During the pre-growth heating, the silicon substrate is attacked by phosphorus species. The insert shows a dark field image of the silicon crystal. The BP/Si interface consists of hillocks with (111) facets.
microscope image is built using only electrons that are diffracted by the silicon lattice. Whereas the samples grown following normal procedure (short delay) showed interface roughness of smaller than 7 Å, this sample shows an interface with hillocks of several nanometers.

4.4.2 Optical characterization

The optical reflection spectrum of the as-deposited structures has been recorded using a spectrophotometer. However, due to the interference patterns and the absorption of the silicon substrate, no detailed absorption behavior can be derived from reflection spectra only. More detailed information on the transitions in the material can be obtained from combined

Figure 4-9. Mott-Schottky plot of an n-type Si / n-type BP / 0.1 M NaOH junction (open triangles) and a n-type Si / p-type BP / 0.1 M NaOH junction (closed triangles) recorded at 10 kHz. The donor, and acceptor densities of the BP epilayers are $4 \times 10^{18}$ and $6 \times 10^{19}$ cm$^{-3}$, respectively.
reflection-transmission spectra of samples having the silicon substrate (partially) removed. For this purpose, BP films have been deposited on silicon wafer material that is provided with a nitride back-coating to be used as an etching mask.

However, the nitride coating appears to be etched by the high temperature hydrogen ambient during deposition. As an alternative, BP films have been completely separated from the silicon substrate by wet-etching in a HF/HNO$_3$/H$_2$O solution. Small, rectangular sheets of BP have been gathered, which show strong bending when dried (typical bending radius of a few cm). We have not been able to extract reliable optical data from these samples.

4.4.3 Electrical characterization

The Seebeck coefficient is found to be negative for all cubic BP films where no Si doping has been applied. Negative Seebeck coefficients are also found for films grown with gas mixtures including 0.04 Torr SiH$_4$ on p-type silicon. The films grown on n-type substrates using 0.062 Torr SiH$_4$ partial pressure show no detectable thermopower.

To determine the carrier concentration in the film, the small ac signal response has been studied by mounting samples in a three electrode electrochemical cell. The impedance spectrum of the electrode shows a semicircle, which can be modeled by a resistor R parallel to a constant phase element Q. Q has an impedance given by $Z_Q = K^{-1} (j\omega)^n$. The factor $n$ of the latter equals 0.9, which justifies the use of Q for the differential space charge capacitance $C_{sc}$. In Figure 4-9 typical Mott-Schottky plots of $C^2$ vs. the polarization are shown for electrodes with an n-type film of BP and a Si doped (p-type) film. These plots are reproduced in the range of 1-25 kHz.

The dark current-voltage characteristics of the heterostructures are presented in Figure 4-10. There is a distinct diode behavior for BP and Si-doped BP on p-type silicon, although
the reverse current is rather high. If the diode is illuminated by light, a change in the carrier concentrations is expected. However, due to the high leakage current, the difference in current-voltage characteristics in dark and illuminated conditions is small. The open circuit voltages induced by illumination are 0.5 V for p-Si / n-BP, -0.3 V for n-Si / p-BP, and 0.08 V for the n-Si / n-BP junction.

Recordings of the surface potentials during the illumination sequence are shown in Figure 4-11. For each graph, the steps in the illumination sequence are indicated, and are accompanied with a change in the slope of the surface potential. For both anisotype junctions (a and b), a strong effect of illumination on the surface voltage is found, in the order of several tenths of volts. In contrast, illumination of the n-BP/n-Si structure shows surface photo-voltage of only a few mV (c). Reduction of the light intensity lowers the response, indicating that saturation has not been reached. However, the Si-doped BP structure is close to saturation, because only a small difference exists between the 100% and the 60% illumination levels (a). At the highest illumination level of this structure, the red-filter is inserted again at 185 s. and the illumination is prolonged for 35 seconds, in order to demonstrate the transient behavior close to saturation.

4.5 Discussion

4.5.1 Growth and structure of the Si/BP interface

The as-grown BP films show a roughness up to a few nanometers. This is typical for CVD-grown layers in a reaction-limited regime. Surface species move around to find the low-energy locations, typically at steps in the crystal surface. However, surfaces of films with thicknesses over 1 μm tend to roughen considerably. This phenomenon is common in the epitaxy of lattice mismatched materials [29], in which tensile (or, in other cases, compressive) strain causes the surface to roughen after a certain film thickness.

In these films considerable residual strain remains, which can be deduced from the closely spaced fringes in figure 4-5. These fringes are due to small local shifts in the electron diffraction angle, caused by mechanical bending of the thinned sample and local misalignment between the electron beam and the atomic planes.
The lattice mismatch is accommodated by interstitial planes, starting in the first few atomic planes of the BP film. In addition, anti-phase domains are present. This type of stacking fault is common in epitaxy where a binary compound is deposited on a non-polar crystal.

In spite of the large lattice mismatch, epitaxial films of BP can be grown on silicon. An effective route to accommodate this difference in crystal dimensions must be present. This is achieved by the creation of a large number of extra planes in the first few atomic layers of BP (Figure 4-6). The ratio of the lattice parameters is such, that the width of five planes in the silicon lattice equals six planes in the BP crystal. Within the first five or six atomic layers of the BP film, the mismatch is accommodated in this manner, and the remaining mismatch is only 0.2 %.

However, the films show a large number of twins, which are visible in both Figure 4-5 and 6 as sharp lines making a 60° angle with the interface. Once formed, a twin boundary extends through the epitaxial film, until it crosses another and both are extinguished. Starting with the (100) orientation of the substrate, the twinning leads to the occurrence of crystal orientations different from the (100). These can be found by a 60° rotation around \{111\}.
(with reference to (100)). The corresponding orientations are (100), (-100), (22-1), and (-2-21) [30]. In Figure 4-7, all of these can be found. The distance between (22-1) planes is 1.496 Å, corresponding to a X-ray diffraction at 62° 2θ.

The influence of phosphorus species present in the reactor during the pre-growth heating can be seen in the dark field images of Figure 4-8. Although initially flat, the silicon/boron phosphide interface is extremely roughened. Hillocks as high as 20 nm, terminated by (111) planes, can be seen. This is most likely the result of an etching mechanism, since these planes, being the closest-packed, are the slowest etched in all III-V compound semiconductors. Similar etching of Si(100) surfaces is observed in the CVD of epitaxial GaAs on Si [31]. In that paper, the roughening of the substrate is related to the intentional presence of AsH₃ during heat pretreatment. However, the exact mechanism is still unclear.

4.5.2 Electrical characterization of the BP films

The determination of the sign of the Seebeck coefficient of a semiconducting film on a substrate of the opposite conduction type is not affected by the substrate. A flow of charge carriers via the substrate cannot take place due to the rectifying nature of one of the two interface crossings. In the case of an isotype junction, the influence of the substrate will not change the sign of the Seebeck coefficient. The magnitude of this coefficient, however, is more complicated, and will not be discussed in this paper.

The negative sign of the Seebeck coefficient for all crystalline films, grown without SiH₄ in the gas mixture, confirms boron phosphide to be an n-type semiconductor. The silicon-doped samples produced inconclusive results, showing that the silicon induces changes in the electrical behaviour of the BP film. More details can be obtained by analyzing the electrochemical data. Goossens [11] reported a concise electrochemical study of the BP / Si electrodes. He found that the depletion layer, induced by a rectifying liquid contact, is almost entirely restricted to the top of the BP film. The current-voltage characteristics of the structures supplied with ohmic In-Ga contacts show high leakage currents. This leads us to conclude that in the electrochemical cell the voltage drop is located at the liquid junction, when this junction is in reverse bias. The electric field extends from the liquid interface into the BP film. Therefore, the plots of Figure 4-9 reflect the capacitance of the BP / electrolyte interface. The depth of the depletion layer in the BP is dependant on the electric field, causing the voltage dependency of the capacitance. Neglecting other voltage dependant effects in this capacitance, the Mott-Schottky relation [32, 33]
\[ C^{-2} = \frac{2}{\varepsilon_r \varepsilon_0 eN A^2} \left( \phi_{sc} - \frac{kT}{e} \right) \]  

(4-2),

applies, in which \( N \) denotes the effective doping concentration, \( C \) the depletion layer capacitance, \( A \) the contact area of the junction, and \( \phi_{sc} \) the voltage drop over the space charge. The latter is the applied voltage minus the flat band potential. Other symbols have their usual meaning.

The slope of the plots can be used to derive the effective doping density \( N \) of the BP film. Because the films are smooth, the effective area can be approximated by the area of the wetted BP surface, being 7 mm². Taking a value of 11 for the dielectric constant of BP [14], the n-type films show a donor density of \( 4 \times 10^{18} \) cm\(^{-3} \), whereas an acceptor density of \( 6 \times 10^{19} \) cm\(^{-3} \) is found for the Si-doped film on n-Si substrates. For these films, the incorporated Si acts as an acceptor dopant, and it is possible to achieve a dopant density to overcompensate the intrinsic donor density. For the silicon doped BP films on n-type Si substrates, this is not achieved. It is possible that the concentration of Si species inside the BP lattice is too low, but there is a more convincing explanation. In principle, silicon is an amphoteric dopant in III-V compounds, able to act either as a donor or an acceptor. The formation of an isotype junction is expected to be favourable as it lowers the internal electric field. If this is true for the formation of Si/BP heterostructures, the anisotype pBP/nSi structure cannot be achieved by silicon doping.

A consequence of this mechanism concerns possible autodoping, where Si atoms diffuse out of the substrate material into the BP film during growth. This contamination is an unintentional doping effect that can only be avoided by a considerable lowering of the deposition temperature. Following our line of reasoning, autodoping will not cause an anisotype junction.

The flatband potential, at which no space charge region is present, can be derived from the intercept of the potential axis, provided that the Helmholtz capacitance is large. The intercepts lie at -1.5 V and 4.0 V vs. Standard Calomel Electrode (SCE), for the n- and p-type films, respectively. If the fermi levels of both conductivity types are very close to the appropriate band edges, which is the case due to the high doping densities, the flatband potentials of the conductivity types are separated by a value corresponding to the bandgap. Clearly, in this study the potential drop over the Helmholtz layer must be taken into account. De Gryse [34] showed the distribution of the applied voltage at the intercept \( \Delta V_0 \) to be
\[ \Delta V_0 = \phi_b + \frac{kT}{e} - 2\pi\epsilon_r\epsilon_0 e \frac{N}{C_H^2} \]  \hspace{1cm} (4-3),

where \( C_H \) is the Helmholtz capacitance, and \( \phi_b \) the flatband potential. Goossens showed the potential drop over the Helmholtz layer in the n-BP/NaOH system to be negligible. As a consequence, the voltage drop over the p-BP/NaOH system at flatband is 3.5 V. The Helmholtz capacitance is found to be 35 \( \mu \)Fcm\(^{-2}\). This value agrees with that found for n-BP in acid electrolytes [35].

### 4.5.3 The electronic structure of iso- and anisotype BP/Si junctions

Structural analysis shows the BP/Si heterojunction containing a large number of point defects.

![Band diagram based on the Anderson model, taking into account that the BP is doped much stronger than the Si.](image)

![Band diagram derived from Fermi level pinning at midgap, taking into account the high doping density of BP.](image)

They are expected to generate abundant energy levels inside the forbidden gap, and therefore Fermi level pinning is likely. In addition, interdiffusion must be expected. If this diffusion is not restricted to the immediate interface, in theory a stack of junctions could be formed [8]. For the structures in this investigation, the structural analysis shows that all significant disturbance of the lattice is restricted to an interface region of a few layers of atoms, except for the twinning of the BP. Typical diffusion rates imply that interdiffusion also will be restricted to a few nanometers around the interface.

In this discussion we combine all these effects to a continuous distribution of gap states at a single junction located at the BP/Si interface. Then both acceptor- and donor-like
states are present and the Fermi level can be pinned. If the concentration of interface states is high compared to the doping of the bulk semiconductor, this pinning will take place at the center of mass of the surface-state distribution. Assuming the creation of gap states to be independent of the conductivity type of the silicon substrate, the position of the Fermi level at the interface is identical for each of the four possible junctions.

The differences in band alignment models are best illustrated by discussing the behavior of the charge carriers generated by illumination of the junction. For this, we must adjust the band diagram based on the Anderson model to the high doping density determined by the Mott-Schottky analysis. Because the doping level of the silicon is only $10^{17}$ cm$^{-3}$, Eq. 4-1 predicts the band bending to be almost completely restricted to the Si side of the junction. Inside the silicon close to p-type BP, the valence band crosses the Fermi level. Here, the upward bending will not proceed due to hole accumulation. According to Eq. 4-1, the band bending in the BP will be slightly increased as a consequence. The adjusted Anderson band diagram is shown in Figure 4-12. The adjustment that must be made to the band diagrams derived for Fermi level pinning at midgap is shown in Figure 4-13. The region in the BP where band bending is situated, is narrow compared to the region in the silicon. This only has implications for the n-BP/p-Si structure (compare Figure 4-2d and 4-13d), because now tunneling of photo-electrons from the silicon becomes conceivable.

To compare the band diagrams of both models, we will consider the electronic behavior that can be derived from the diagrams. For the anisotype structures, the overall effect for both models will be similar if tunneling can take place. Tunneling is likely to occur because of the steep bands in the BP close to the interface. The isotype structures predict quite different effects. For the majority carriers, the Anderson model predicts a smooth transition from one material to the other. The midgap pinning, however, poses a barrier at the interface. The behavior can be illustrated by considering the photovoltaic effect for these structures.

If the junction is illuminated with light of sufficient energy, a large increase in the concentration of minority carriers is generated by absorption. Considering the limited thickness of the epitaxial BP film, and its relatively large bandgap, practically all charge carriers are generated in the silicon. If there is a band bending, the carriers will be separated and both electrons and holes will drift according to the internal electric field, associated with the band bending. In the case of anisotype junctions, both models predict a photovoltage to build up, in spite of the barrier for minority carriers generated in the silicon. However, for the isotype junctions the models diverge. According to the Anderson model (Figure 4-12), there is a drive for the photocarriers away from the interface into the silicon. In case Fermi level
pinning at midgap position occurs (Figure 4-13) photo carriers are driven towards the interface where recombination will take place. The value of 0.08 V found for the n-Si/n-BP structure suggests the applicability of the Anderson model. Unfortunately, the case of the p-type isojunction would have shown a stronger effect in an experiment.

4.5.4 Current-voltage characteristics

While the band bending depends on the voltage applied over the structure, we assume that the band offsets and interface defect density are not affected by an external voltage. Since the metal contacts on both semiconductors are ohmic, rectifying behavior and photovoltage affects are due to the positions of the bands around the interface of the heterojunction.

The current-voltage curves measured for the n-BP/p-Si structure show a rectifying behavior. However, a significant leakage current is present. Obviously, this is due to the large number of interface gap states originating from the atomic disarrangement at the junction.

It is difficult to derive quantitative information on band alignment from these data because of the high leakage current. However, the open circuit voltage, generated by illumination, presents a minimal value for the total band bending around the junction. Experiments show that the Si side of the n-BP/p-Si sample acquires a positive potential of 0.5 V with respect to the BP-side. This is in agreement with the band diagrams of both Figures 4-12d and 2d. Photoelectrons are created in the silicon, they diffuse towards the depletion layer and the band bending drives them into the BP. The redistribution of charge carriers causes the photovoltage, and a reduction of band bending by the same amount. Therefore, the band bending in unilluminated n-BP/p-Si must be at least -0.5 eV, going from p-Si to n-BP.

n-Si substrates covered by Si-doped BP show photovoltage of the opposite sign. This suggests that the photoelectrons, created in the silicon, flow away from the interface, building the field observed. This observation also agrees with the band bending in the band diagram deduced from both models (Figures 4-12c and 4-2c).

Finally, the current-voltage curve of the n-BP/n-Si structure shows only a slight deviation from linearity. The open circuit voltage of 0.08 V (Si positive with respect to BP) indicates only a slight drive for photoholes away from the interface. This does not collaborate with either model. However, there are two possible explanations due to the fact that the conduction band minimum is almost completely flat over the entire heterojunction. Band bending direction will be strongly affected by the doping level in both semiconductors. A drive for holes into the silicon is present if the conduction band of the bulk BP is closer to the
fermi level than that in the bulk silicon. Secondly, if the donor density in the silicon increases towards the interface (due to phosphorus indiffusion), a slight bending will be present in the silicon, which forms a small drive for holes in the direction observed. It is practically impossible to obtain data sufficiently precise to resolve this matter.

4.5.5 Surface-photovoltage characteristics

The surface-photovoltage signals, as measured with the Kelvin probe, also provide quantitative information on the total band bending in the material. Illumination raises the concentrations of the minority charge carriers, causing a gradual shift in the quasi Fermi levels. In the depletion regions the carriers are separated and drift according to the slope of the band edges. Saturation is reached when the summation of all band bending is minimized.

The Kelvin probe recordings of the n-n structure show that there is only a small effect of illumination on the surface potential. This is in accordance with the Anderson model. The transient behavior of the surface potential upon illumination which is observed requires a more detailed and optimized study.

The results obtained for the anisotype junctions cannot be used for resolving the two models. There is no indication that the influence of the long pass filter can be attributed to other mechanisms than to the reduction of the light intensity. Illumination with long wavelength light (absorption not possible in the bulk of the BP) does not show a different response than the white-light illumination. The p-Si/n-BP structure responds fast and significantly to the illumination sequence. It does not reach saturation even at the highest level of illumination. The total band bending in this structure is at least 0.45 eV.

For the n-Si/p-BP structure the total band bending is 0.52 eV, because saturation is reached at the strongest illumination. Only a small increase in voltage is observed between the illumination with 60% and 100% white light. In addition, only a transient increase is observed at 100% illumination, if the red filter is removed. The transient is reversed upon inserting the red filter. There are two effects that can be the cause of this behavior. Generation of hot charge carriers, which will increase the photocurrent through possible barriers at the junction. This does not seem to play a role. Secondly, the effect of the red filter is a shift in the absorption depth profile. With the red filter in place, the photocarriers are generated in the silicon, the interface states and the surface states. Upon removing, the bulk BP starts absorbing as well. This is only a small effect though, due to the limited thickness of the BP layer. However, the generation of carriers in the silicon is shifted towards the interface due to the higher absorption coefficient of silicon at higher photon energies. Carriers in the depletion

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region will drift towards the junction, whereas carriers generated deeper in the silicon, will reach this layer only after diffusing. The data suggest that these changes in photocarrier generation do not influence the saturation condition qualitatively. They do have an effect on the transients, which is probably due to the diffusion of holes in the bulk of the silicon. The p-Si/n-BP structure does not show this slow response because the diffusion of electrons is much faster.

4.6 Conclusions

The epitaxial growth of boron phosphide on silicon substrates by reduction of bromides in hydrogen is investigated. Although the Si/BP system implies a large lattice mismatch, epitaxial growth takes place. The mismatch is accommodated very effectively by interstitial planes in the BP lattice. Epitaxial films are smooth below 1 micrometer thickness. Beyond, the surface starts to roughen. Whereas substrate exposure to BBr3 leads to boron rich amorphous material, prolonged exposure to phosphorous species prior to BP growth must be avoided as well: At typical growth temperature, a H2 PBr3 mixture causes a strong roughening of the substrate.

Electrochemical techniques have been used to investigate the BP films. The BP films obtained in this system are all n-type, typical effective donor concentration of 4x10^{18} cm^{-3}. Samples grown on p-type silicon with additional SiH4 show p-type conductivity, with typical effective acceptor concentration of 6x10^{19} cm^{-3}. However, BP grown on n-type silicon under identical conditions is n-type. An increase of the SiH4 dopant gas concentration results in the formation of the amorphous B,P. The Si, in principle an amphoteric dopant, only acts as an effective acceptor if the substrate is p-type.

Two models have been used to construct qualitative band diagrams of the Si/BP junction: the Anderson model, and a model assuming Fermilevel pinning at midgap. The current-voltage behavior of the three heterostructures that are obtained, i.e. p- and n-type BP on p-type silicon, and n-type BP on n-type silicon, show strong recombination at the junction. The open circuit voltage upon illumination indicates a band line-up in agreement with the Anderson model.
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Chapter 5 *

PHOTO- AND ELECTROREFLECTANCE OF CUBIC BORON PHOSPHIDE

In order to reveal the band structure of the III-V semiconductor cubic boron phosphide a photo- and electroreflectance study has been undertaken. Towards this end, epitaxial thin films of this III-V semiconductor are grown on silicon (100) by chemical vapor deposition. Both modulated reflectance techniques reveal a critical point at 4.25 eV. This value of the first direct transition is more than 1 eV lower than previous reports, which are based on transmission spectra.

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5.1 Introduction

Boron phosphide (BP) is a III-V semiconductor with a zinc-blende crystal structure and an indirect band gap of \(2.0\) eV [1]. Its mechanical and chemical properties allow classification as a refractory material [2]. Recently, BP has been investigated as a protecting optical window for silicon photo-electrochemical cells [3]. A recent review of the material has been reported by Kumashiro [4]. Although cubic BP is almost fully covalent (e.g., even more covalent than SiC), the band diagram is similar to that of other III-V compounds [5]. At present, there is little experimental data available on the band structure of BP. For thin polycrystalline films, Stone and Hill [6] have reported a direct bandgap of almost \(6\) eV and a shoulder in the transmission spectrum at \(2\) eV. Using small BP crystals Archer et al. [7] have assigned the latter to the fundamental, indirect band gap of \(2.02\pm0.05\) eV. The optical reflectance spectrum reported by Wang and co-workers [8] shows a weak maximum at \(5.0\) eV and a strong maximum at \(6.9\) eV, tentatively attributed to transitions \(\Gamma_{15}-\Gamma_{15}\) and \(X_{5}-X_{1}\).

In order to clarify the nature of the band edge of BP, a study is performed using modulation spectroscopy techniques. This class of techniques is very powerful for the investigation of so-called critical points in the band structure of solids. In this paper, the first electrolyte electroreflectance (EER) and photoreflectance (PR) spectra of BP are presented.

Thin films of epitaxial boron phosphide, grown on the \((100)\) face of silicon are investigated. The spectra have been recorded in the energy range from the indirect band gap of BP \((2\) eV) up to \(5\) eV. They show several features, of which the most dominant one can be attributed to a critical point at \(4.25\) eV that is assigned here to the lowest direct valence-conduction band separation.

5.2 Experimental aspects

Samples were prepared in an induction heated, cold wall chemical vapor deposition set-up, using the precursors \(\text{BBR}_3\) and \(\text{PBr}_3\) diluted in \(\text{H}_2\). Reaction took place on thoroughly cleaned pieces of Si wafer, placed on top of a graphite susceptor, under atmospheric pressure at temperatures around \(900^\circ\text{C}\). Prior to the deposition the Si substrates were heated to \(950^\circ\text{C}\) in hydrogen to obtain a reconstructed H-terminated surface. Typical gas flow rates were \(1800\) ml/min. with partial pressures of 3 and 0.3 Torr for \(\text{PBr}_3\) and \(\text{BBR}_3\), respectively. Typical layer
thicknesses were between 0.2 and 1.5 μm at a growth rate of 0.6 μm/hr. X-ray diffraction and high-resolution TEM (Philips CM30-UT/FEG) analysis were used to determine the crystallinity of the epitaxial layers. A reflection spectrum of the Si/BP structure was recorded using a photospectrometer (Varian UV-VIS-NIR) with 1 nm spectral bandwidth.

Two types of modulation spectroscopy have been performed, EER and PR. In the first method, the sample is periodically perturbed by a modulation voltage parallel to the probing light beam. In the second method, the perturbation is caused by periodic changes in the charge carrier concentration. While PR is a contactless method, for EER analysis, a transparent, rectifying contact is required at the BP/electrolyte interface. This is accomplished in a three-electrode electrochemical cell, filled with an indifferent electrolyte (0.1 M NaOH). Potentials are measured with reference to a saturated calomel electrode (SCE). A eutectic solution of In/Ga on the silicon back-side acts as ohmic back-contact. A potentiostat (Solartron 1286) controlled the potential of the BP/Si sample. To verify that the active junction is located at the BP/electrolyte interface, C-V analysis is performed using a frequency response analyzer at a frequency of 10 kHz. For EER the ac modulation is typically 70 Hz with an amplitude of 100 mV. The reflected light is detected by a photomultiplier and fed into a lock-in amplifier and a multimeter to measure the modulated and total reflection. A 150 Watt Xe-lamp and grating monochromator provided monochromatic light with a resolution of 5 nm. With the aid of high-pass filter glasses (Schott), an energy window from 2 to 5 eV could be covered. A stepped wavelength scan was performed, using computer control of the monochromator, the multimeter, and the lock-in amplifier. The photoreflectance measurements were performed in air at room temperature using the same light probing set-up. The sample was mounted on a holder, and irradiated by a chopped laser beam of 543.5 nm (2.28 eV) light (Melles Griot 5 mW

Figure 5-1. Transmission Electron Micrograph of a 180 nm thick epitaxial film of BP on Si(100).
HeNe Laser), using a HMS model 220 light beam chopper. The lock-in amplifier measured the ac part of the amplified photomultiplier signal phase-locked to the chopped laser beam (typically 900 Hz).

5.3 Structural analysis

In spite of the large lattice mismatch, BP can grow on Si(100) substrates epitaxially. BP films of a few hundred nanometers are smooth, whereas with larger film thicknesses, the surface tends to roughen. This phenomenon is common in the epitaxy of lattice mismatched materials [9], in which tensile (or, in other cases, compressive) strain causes the surface to roughen after a certain film thickness. A transsection of a 180 nm film of epitaxial BP on Si(100) is shown in Figure 5-1. On both sides of the interface, fringes in the electron image reveal considerable strain, which is caused by the difference in thermal expansion of both materials. Figure 5-2 is a high resolution image of the BP/Si interface, and shows that the BP crystal contains additional planes to allow for the large lattice mismatch between the silicon (a=5.43 Å) and the BP lattice (a=4.53 Å). Five nanometers away from the silicon surface, the BP lattice parameter deviates only 1% from its bulk value. Since the ratio between the lattices of Si and BP is very close to 6 : 5, we postulate that the mismatch can be accommodated very effectively by introducing one extra atomic plane for every five Si planes. Although a reconstructed, H-terminated silicon surface is used to reduce anti-phase boundaries, the observed hillocks are very large. Similar roughening is observed in the CVD of epitaxial GaAs on Si [10]. There the effect has been attributed to the interaction of the AsH$_3$ with the substrate prior to the epitaxial growth. In our case, the presence of phosphorus on the
susceptor support, could result in a similar effect during the initial heat treatment of the Si substrate.

The reflection spectrum of a sample with a thin BP film is shown in Figure 5-3. The main features at the low energy side are caused by interference within the BP layer. Since the index of refraction 3.1 throughout the visible region, a layer thickness of 450 nm is found. The high energy part of the spectrum shows a strong minimum at 4.8 eV, which is corresponding to the weak maximum reported by Wang et al. [8].

### 5.4 Results and Discussion

A typical result of capacitance-voltage profiling, performed in the electrochemical cell on a 450-nm-thick BP film, is presented in Figure 5-4. The donor density $N_D$ can be determined from the slope of this plot using the Mott-Schottky relation:

$$\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon_r \varepsilon_0 e N_D A^2} \left( \frac{\Delta V_{sc}}{e} - \frac{kT}{e} \right)$$

(5-1)

in which $C_{sc}$ is the capacitance of the space charge layer related to a potential drop $\Delta V_{sc}$ inside the semiconductor electrode. $A$ is the contact area of the space charge layer with the
electrolyte, and $N_D$ is the donor density in the material. The relative dielectric constant $\varepsilon_r$ of BP is 11 [1]. Other symbols have their usual meaning. A donor density of $1.5 \times 10^{18}$ cm$^{-3}$ is found for the sample of Figure 5-4; this value is typical under the growth conditions mentioned. The change in slope signifies a change in the donor concentration, situated close to the BP surface. Since the donor has been identified as a surplus of P atoms [4], this change is likely to be caused by outdiffusion of P-atoms during the cooldown after the synthesis. The bulk donor density is higher, namely $5.7 \times 10^{18}$ cm$^{-3}$, as can be found from the slope at the positive potential side of Figure 5-4. Further investigation of this effect is called for. In this type of C-V analysis, the flat band potential is found by extrapolation of the linear $C^2$ vs $V$ plot to the potential axis. This intercept lies at -1.4 V vs SCE ($pH=13$). Considering the donor density found, the thickness of the depletion layer is in the order of tens of nanometers, and does not reach the Si/BP interface. A more detailed investigation on the behavior of the Si/BP electrode has been reported by Goossens et al. [3].

Since the voltage modulation takes place in the BP space charge region at the BP/electrolyte interface, modulation in the reflectance is caused by the influence of the changing electric field on the BP energy diagram. The EER spectrum of 1.5-μm-thick films is presented in Figure 5-5 (top). The shape of the spectrum does not change upon variation of the bias and the ac modulation potential (ranging from -0.5 to 0.5 V vs SCE and 50 to 200 mV, respectively), as predicted by theory [11]. The amplitude of the EER signal scales linearly with the amplitude of the ac potential.

Because of the strain in the Si/BP interface, it is possible to remove the BP film by applying a voltage pulse over the cell. After this pulse the EER spectrum shows the critical point of Si at 3.4 eV [11], while the critical point above 4 eV has disappeared. Since the

![Figure 5-5. Modulated reflectance spectra of BP grown on Si(100): Top: EER spectrum of a 1.5 μm-thick film. The critical energy lies close to the zero crossing at 4.3 eV. Middle: EER spectrum of a 450 nm thin film. The critical energy at 4.35 eV is clearly visible. Additional features are interference effects. Bottom: PR spectrum of a 450 nm thin film.](image)
roughness of the thick films reduces the specular reflection, and thereby limits the energy window in which the signal to noise ratio is satisfactory, thin smooth samples have been prepared. A typical EER spectrum of those samples is shown in Figure 5-5 (middle).

If the perturbation is imposed by a chopped laser beam of photons of energy above band gap, the photoreflectance spectrum of Figure 5-5 (bottom) results. For thin smooth films of BP, the scatter of the laser beam into the photomultiplier is in the order of 50% of the PR peak maximum. This constant signal has been subtracted from the ac reflectance before division by the total reflectance.

As pointed out by Aspnes [11], photo- and electoreflectance spectra can be interpreted as the third derivative of the dielectric function of the material. Under low-field conditions, the form of the spectrum around a critical point obeys the following relationship

\[
\frac{dR}{R} = \text{Re}\{ (E_{ph} - E_c + i\Gamma)^{-n} C e^{-i\theta} \} \tag{5-2}
\]

in which \(dR\) represents the perturbed part of the reflectance signal \(R\), the energies \(E_{ph}\) and \(E_c\) are those of the incident photons and the band separation at the critical point, respectively. \(\Gamma\) is the broadening parameter, and \(n\) depends on the dimension of the critical point: \(n=3\) and \(n=5/2\) for 2-dimensional and 3-dimensional critical points, respectively. \(C\) and \(\theta\) are the amplitude and phase factors; the latter determines the asymmetry of the line shape. There is excellent agreement between the photoreflectance and electoreflectance spectra, although no interference effects are observed in the PR signal (see below). The spectrum around 4.3 eV has been fitted to equation (2) and the results are collected in Table 5-I. The best fit for the EER spectrum of a thin BP film is considerably worse than that for its PR spectrum and that for the EER spectrum of a thick BP film. The EER spectrum of thin BP films is a convolution of its EER spectrum and its interference spectrum.

**Table 5-I.** Best fit parameters from Equation 2 on the three different spectra of Figure 5-5.

<table>
<thead>
<tr>
<th></th>
<th>EER thick film</th>
<th>EER thin film</th>
<th>PR thin film</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E) (eV)</td>
<td>4.25</td>
<td>4.35</td>
<td>4.25</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>0.6</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>(C)</td>
<td>0.1</td>
<td>-0.05</td>
<td>-0.18</td>
</tr>
<tr>
<td>(\theta)</td>
<td>-0.7</td>
<td>-0.35</td>
<td>-1.1</td>
</tr>
</tbody>
</table>

72
Although the interference affects both the total reflection and the ac reflection, it does not cancel out in the EER spectrum. The reason is that light absorption is not linear, and that the space charge layer does not coincide with the entire film in which the interference pattern is created. The PR spectrum taken from samples of the same thickness, does not show this behavior. In this case the perturbation takes place in the entire BP film, which coincides with the origin of the interference.

An EER-voltammogram (Figure 5-6) is recorded by fixing the probing beam at the peak position of 4.0 eV, and scanning the cell bias; the ac modulation is kept at 100 mV. The magnitude of the EER signal drops linearly with the potential drop over the depletion layer. Upon scanning through flat band the electric field is reversed, and a zero-crossing in the EER-amplitude is observed. The zero-crossing confirms the flat band potential of -1.4 V vs. SCE, as found with C-V profiling (Figure 5-4).

![Diagram](image)

Figure 5-6. Dependence of EER amplitude at 4.0 eV on the bias potential. The zero crossing at -1.4 V coincides with the flatband potential derived from Figure 5-4.

5.5 Conclusions

Both reflectance methods provide evidence of a critical energy at 4.25 eV, which we assign to the lowest direct band-to-band transition of BP. Previously reported values for the direct bandgap are overestimated. The flat band potential, determined to be -1.4 V vs SCE in pH=13 by Mott-Schottky analysis, is reproduced by electrolyte electroreflectance voltammetry. The EER spectrum of BP films of 450 nm thickness shows additional features at lower energies.
originating from interference effects. They are visible in the EER spectrum because the depletion layer, in which the signal is produced, does not coincide with the entire BP film, in which the interference takes place. The oscillations are not present in photoreflectance spectra, because in this technique the modulation is applied uniformly over the film.

5.6 Acknowledgements

This investigation was financially supported by the Dutch National Foundation for Scientific Research, section SON. A.G. kindly acknowledges the Royal Netherlands Academy of Arts and Sciences for his fellowship. The high-resolution TEM analysis was performed at the National Center for HREM in Delft.
References


Chapter 6 *

LARGE SURFACE AREA BORON PHOSPHIDE LIQUID JUNCTION SOLAR CELLS

A new semiconductor electrode for sensitized liquid junction photovoltaic solar cells is demonstrated. By making use of Chemical Vapor Deposition, a graphite substrate is covered with a nanostructured thin film, consisting of whiskers of boron phosphide (BP), which are sensitized by amorphous boron subphosphide (B,P). To obtain the two different morphologies of boron phosphide, the partial pressure of the boron precursor is changed during CVD synthesis. The optical properties of amorphous B,P thin films on quartz substrates have been investigated and it is found that the absorption edge is dependent on the boron content. Photocurrent action spectra of sensitized nanostructured films show a mobility edge of 1.5 eV, which is well below the absorption edge of 2.0 eV of crystalline boron phosphide.

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Synthesis and optoelectronic characterization of boron phosphide
6.1 Introduction

Due to its excellent chemical and mechanical stability boron phosphide (BP) is an interesting semiconductor for application in liquid junction photovoltaic (PV) solar cells. Its 2.0 eV indirect band gap prevents its direct use in PV cells, but a film of boron phosphide on silicon can act as a high energy photon absorber and at the same time as protecting window to prevent the etching of silicon [1]. The photo-electrochemical behavior of epitaxial layers of BP grown on Si has been reported by Goossens et al. [2]. As a continuation of these investigations we demonstrate the use of nanostructured heterojunctions consisting of different morphologies of boron phosphide as a photoelectrode.

This approach is an inorganic variation of the "Grätzel-type" photo-electrochemical solar cell [3], which combines the high absorption coefficient of a (dye) sensitizier with a large surface area of a nanostructured wide band gap semiconductor, such as TiO$_2$, ZnO, or SnO$_2$. Over the past years, this concept has gained increasing interest as a competitive alternative for polycrystalline and amorphous silicon PV cells. The porous oxide semiconductor film is synthesized by sintering crystalline particles until an optimum in surface area and conductivity is reached. However, the conductivity of these nanostructures is rather poor because of the numerous grain boundaries. In contrast to the sintering of metal-oxide nanoparticles, porous semiconducting films of boron phosphide can be obtained by Chemical Vapor Deposition in the form of whiskers. Because of the single crystalline nature of the whiskers, combined with the strong anisotropy in dimensions, the grain boundary crossings for charge carriers traveling from the electrolyte to the substrate is minimized without the loss of active area. By covering these whiskers with a suitable sensitizing material, light absorption is enhanced, especially at longer wavelengths. Here, the sensitizer is formed by a thin layer of amorphous B$_x$P (x ≥ 3). This layer can be deposited immediately after whisker growth simply by changing the growth conditions.

Little is known of the properties of the amorphous boron subphosphide. It shows semiconducting properties, and has an optical band gap between 0.5 and 1.7 eV, depending on the stoichiometry. Kelder [4] showed that the B/P-ratio is larger than 3 for B$_x$P synthesized with hot-wall atmospheric pressure CVD and PB$_3$ and BB$_3$ as precursors. B$_x$P has been under investigation for erosion protecting anti-reflection coatings in infra-red detection systems [5] and may form a good alternative for diamond-like carbon. Whereas its
subbandgap absorption is very low, its high absorption coefficient in the visible range is a strong incentive to investigate this material for thin film solar cell application. However, the high resistivity of pin-hole free films frustrates its direct use in solid solar cells [6, 7]. In this chapter, we demonstrate that B$_x$P can be used as a sensitizer in liquid junction solar cells. Both nanostructured BP and amorphous B$_x$P are grown in an atmospheric pressure chemical vapor deposition systems. For optical characterization, B$_x$P is grown on quartz substrates. The effect of B$_x$P on the spectral response of the nanostructured BP photoelectrode is shown.

6.2 Experimental Aspects

In this study, boron phosphide films are grown in an induction-heated, cold-wall Atmospheric Pressure Chemical Vapor Deposition (APCVD) reactor. In the gas supply system hydrogen carrier gas is fed through temperature controlled bubblers filled with the liquid precursors BBr$_3$ and PBBr$_3$. To achieve a well defined supply of these precursors, the gases are cooled in reflux coolers. The resulting saturated carrier flows, with precursor pressures corresponding to 3.0 °C and 64.5 °C, respectively, are lead through heated lines to prevent condensation. After diluting these gases in a hydrogen bulk flow, the gases are mixed and fed into a vertical, water-cooled reaction tube (inner diameter 36 mm). Substrates are placed on a graphite susceptor (diameter 30 mm) which is heated by RF induction. The deposition parameters that are varied are the substrate temperature and the ratio of the precursor partial pressures. They
determine the morphology of the growing film. Kelder [4] constructed a CVD-diagram (Figure 6-1) of the H₂-BBr₃-PBr₃-system, the deposition temperature and the BBr₃ mole fraction β of the precursors, span the space in which deposition takes place. Two regimes can be distinguished: low β leads to crystalline BP, in which the atomic fractions are 0.5, whereas high β results in a boron rich amorphous phase (boron atomic fraction > 0.75).

To obtain the anisotropic growth required for large surface area layers, a vapor liquid solid (VLS) mechanism is evoked. For the VLS-growth of BP, either nickel or silver seeds can be used [8]. Recently, we reported on this system [9] and showed that a wide range of whisker diameters can be obtained, depending on the type of seeding metal, the deposition temperature, and the type of substrate (see Table 6-I). To obtain large surface area electrodes, small diameter whiskers are required. Therefore, synthesis is carried out at the relatively low temperature of 900 °C on graphite substrates using nickel seeds which are applied by dipping the substrate in a solution of 0.1 M nickel acetate. During synthesis, the hydrogen flow rate is 1800 ml/min with partial pressures of 3 and 0.3 Torr for PBr₃ and BBr₃, respectively. After rapid growth of a highly porous layer of whiskers, the BBr₃ partial pressure is increased to 5 Torr which shifts the growth into the amorphous regime. A thin layer of BₓP quickly forms on the crystalline whiskers as has been confirmed by scanning electron microscopy.

Table 6-I. Summary of BP whisker formation on graphite, tungsten, and quartz substrates. The gas-flow rates in the reactor are constant and typical deposition time is 20 minutes.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>seed</th>
<th>Temperature</th>
<th>typical diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>Ni</td>
<td>&lt; 930 °C</td>
<td>0.01 - 0.1 μm</td>
</tr>
<tr>
<td>Graphite</td>
<td>Ni</td>
<td>&gt; 940 °C</td>
<td>1 - 5 μm</td>
</tr>
<tr>
<td>Graphite</td>
<td>Ag</td>
<td>880-1000°C</td>
<td>1 - 10 μm</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Ni, Ag</td>
<td>930°C</td>
<td>1 - 5 μm</td>
</tr>
<tr>
<td>Quartz</td>
<td>Ni</td>
<td>880-1000°C</td>
<td>0.1 - 5 μm</td>
</tr>
</tbody>
</table>
In order to study the optical properties of the amorphous boron phosphide, thin films of this material have also been grown on quartz substrates. Prior to deposition, these substrates are cleaned ultrasonically in acetone and ethanol. Most films have been grown in a horizontal hot-wall APCVD reactor with similar gas supply system. Optical characterization of samples from both reactors has been performed by reflection and transmission spectroscopy in a Cary UV-VIS-NIR spectrophotometer, equipped with an integrating sphere. The boron fraction in the solid phase is determined by X-ray Photoelectron Spectroscopy (XPS) performed on the samples grown in the hot wall set-up. In order to obtain reliable data on the bulk composition, an Ar plasma etch was performed.

Optical and electrical properties of the whisker structures are determined by measuring the photocurrent action spectra. A two-electrode electrochemical cell is used with a platinum counter electrode. An aqueous solution of 0.5 M NaSO₄, completed by the K₃Fe(CN)₆ - K₄Fe(CN)₆ redox couple (both 0.1 M), acts as electrolyte. A Solartron 1286 Electrochemical Interface (ECI) is used to control the potential. A 150 Watt Xe-lamp (PTI Model A 1010) combined with grating monochromator (Acton Research SpectraPro-275) and high pass filters (Schott) provided monochromatic light with a resolution of 10 nm. The light is chopped at 70 Hz and a dual phase lock-in amplifier (EG&G 5210) is used to measure the photocurrent. Prior to the scan, the cell is purged with nitrogen to remove oxygen from the electrolyte and the sample surface.

Figure 6-2. Scanning Electron Micrograph of a layer of BP whiskers grown on graphite. Aspect ratios are up to 10,000.

Figure 6-3. High-resolution TEM picture of the side of a small-diameter whisker. Twin planes show as dark lines.
6.3 Results

An image of a CVD film of crystalline BP whiskers is shown in the SEM-micrograph in Figure 6-2. The graphite surface is completely covered with a highly porous layer of whiskers with a diameter of typically between 50 and 100 nm. A high-resolution TEM image of a fraction of a whisker is shown in Figure 6-3. The dark lines inside the crystal and the edges at the whisker surface indicate twinning. Apart from the twin planes, the material is monocrystalline. Electron diffraction shows that growth is exclusively in the <111> direction. Twin planes are (111) and (22-1) and their equivalents. Energy dispersive X-ray analysis does reveal nickel at the graphite substrate, but no detectable trace of the catalyst is found in either the top or the body of the whiskers. The X-ray diffraction pattern of the as grown material proves that the whiskers consist of cubic boron phosphide.

Figure 6-4. Reflection and transmission spectrum of an amorphous B,P films grown at 900 °C on quartz. A distinct absorption edge can be observed in the transmission spectrum. The film thickness (300 nm) is calculated from the interference pattern in the reflection spectrum.
The reflection and transmission spectrum of a typical thin amorphous B,P film grown on a quartz substrate with a thickness of 300 nm is shown in Figure 6-4. In the visible part of the transmission spectrum, a distinct absorption edge can be seen. The XPS spectra show two peaks that remain after the Ar etch. These can be attributed to the phosphorus 2p (129 eV) and boron and phosphorus 2s orbitals (189 eV), respectively. The peak intensities are used to calculate the phosphorus and boron fractions in the solid.

![Graph showing photocurrent action spectrum](image)

**Figure 6-5.** Photocurrent action spectrum of a large surface area liquid junction BP cell: Graphite covered with a highly porous layer of BP whiskers (a), whiskers sensitized with B,P (b). An aqueous electrolyte of 0.5 M NaSO₄ and 0.1 M K₃Fe(CN)₆ / K₄Fe(CN)₆ and a platinum counter electrode are used.

The photocurrents are always anodic, i.e. the photoelectrons flow into the graphite substrate. The photocurrent action spectra of the large surface area BP films are presented in Figure 6-5. The photocurrent from the polycrystalline whiskers (a) without the sensitizer is obtained for photon energies of 2 eV and higher. Nanostructures with the amorphous sensitizer present (b) show a clear shift in photocurrent action spectrum towards lower photon energy. For the sensitized electrodes, the external quantum efficiency has a maximum value of about 3×10⁻³.

### 6.4 Discussion

#### 6.4.1 Whisker growth

During the first step of the synthesis, a layer of randomly oriented whiskers is formed with a vapor-liquid-solid (VLS) mechanism in which the precursor gases are dissolved into molten metal seeds. When saturation is reached inside these droplets, crystallization of BP starts. It is most likely that the basis of the metal droplets will act as nucleation centers, which leads to
the growth of whiskers underneath the droplets. Although growth is very rapid, the whiskers are single crystalline, exhibiting only twins as stacking faults. The small diameter of the BP whiskers grown on graphite with nickel is achieved by preventing coalescence of the seeds. Because nickel acts as a catalyst for the hydrogenation of graphite [10] during pregrowth conditions, holes are created in the graphite, into which the seeds sink. At temperatures exceeding 940 °C, the wettability is much better [11] and larger seeds are produced by coalescence. The axial (VLS) growth mechanism is very effective, and the typical rate is 0.5 μm/min. On the side of the whiskers conventional CVD growth takes place. If the gas mixture is not depleted, this growth occurs at a rate of 0.01 μm/min.

6.4.2 Characterization of amorphous B,
P on quartz
The absorbance of B,
P can be obtained from transmission and reflection spectra by applying the Lambert-Beer relation to a thin, strongly reflecting semiconductor film:

\[
\alpha d = \ln \left( \frac{1 - r^2}{t} \right)
\]  \hspace{1cm} (6-1),

in which the absorption coefficient \( \alpha \) is related to thickness \( d \), and to the reflection and transmission coefficients \( r \) and \( t \), respectively [12]. Using the interference pattern, present in the \( r \) and \( t \) spectra, the film thickness (typically 300 nm) is calculated using a constant value of 11 for the refractive index. Quantitatively, the absorption coefficient is comparable to that of amorphous silicon. To determine the optical band gap from absorption spectra, different models can be used [13-16]. In these models particular assumptions are made for the shape of

Figure 6-6. Determination of the optical gap of various amorphous films of B,
P following Klazes [15]. The insert shows the influence of the boron atomic fraction \( \beta \), as determined by XPS, on this gap. The point at \( \beta = 0.5 \) corresponds to the indirect gap of crystalline films. For amorphous films, the minimum boron content is 0.75, corresponding to \( x = 3 \).
the density of states at the band edges and for the definition of the band gap. The absorption spectra found for amorphous boron phosphide are best fitted by assuming linear band tails, for which the relation

$$\alpha d \propto (h\nu)^{-1} \cdot (h\nu - E_g)^3$$  \hspace{1cm} (6-2),

holds, $E_g$ is the optical band gap and $h\nu$ is the photon energy. The optical gap is determined for a number of samples grown under different conditions. In Figure 6-6 band gaps of samples grown in the hot-wall CVD reactor are related to the boron content determined with XPS. There is a distinct lowering of the optical band gap with increasing boron content.

6.4.3 Photocurrent action spectra

The photocurrent action spectrum of the uncoated whiskers clearly shows an energy edge of 2.0 eV, which is the indirect band gap of crystalline BP [17]. The observation that the photocurrent is anodic corresponds to the n-type conduction of the BP whiskers. This conduction type agrees with previously reported characteristics of (poly-) crystalline BP thin films [2, 18]. Photons of energy above 2.7 eV are absorbed by the electrolyte, and do not reach the semiconductor electrode. The spectrum of the whiskers that are coated with amorphous $B_xP$ shows a response well below 2 eV. Although the sensitivity of the cell is extended to 1.5 eV, the photocurrent at photon energies above 2.1 eV has dropped considerably. In addition, the open circuit voltage is very low (~1 mV). These effects are due to the rise in internal resistance of the electrode, and to electron-hole recombination at the BP/$B_xP$ or $B_xP$/electrolyte interfaces. It is questionable whether amorphous $B_xP$ can be considered a semiconductor; it has a very low conductivity although we found an activation energy for conduction of only 25 meV (in the range 77-300 K). The external quantum efficiency is only about $3 \times 10^{-3}$ which shows that the system is far from being optimized. In particular, the film thickness of the sensitizer $B_xP$ should be reduced. Also contact between the graphite substrate and the redox electrolyte must be further diminished.

There is a marked difference between the optical band gap of the amorphous films grown on quartz and the energy edge observed in the photocurrent action spectra. Apart from the difference between the optical band gap and the mobility edge, which arises from the spatial localization of the band edge levels [16], a lower boron content in $B_xP$ grown on BP compared to that of $B_xP$ grown on quartz under the same CVD conditions is expected. This is
attributed to the relatively long residence time of the gas species inside the porous film of whiskers, which retards the increase of the BBr₃ fraction.

6.5 Summary and Conclusions
A photoelectrochemical cell is constructed making use of a large surface area films of BP whiskers, grown on graphite substrates. The spectral response could be extended to longer wavelengths by applying the amorphous phase of boron phosphide as sensitizer. The optical gap of BₓP is investigated using thin films grown on quartz substrates. A distinct relationship between the boron content and the band gap is found.

Photocurrent action spectra of BP whisker films on graphite show an energy edge of 2.0 eV, concordant to the optical band gap of cubic boron phosphide. Whiskers with a film of amorphous BₓP generate photocurrents at photon energies down to 1.5 eV, demonstrating the sensitization principle of BP-whiskers with amorphous boron phosphide.

6.6 Acknowledgements
This investigation was financially supported by the Netherlands Organization for Scientific Research (NWO), and by the Netherlands Agency for Energy and the Environment (NOVEM). A.G. kindly acknowledges the Royal Netherlands Academy of Arts and Sciences for his fellowship. Data on the hot-wall amorphous BₓP films have been obtained with the help of Dr. E. Kelder.
References

Chapter 7

INVESTIGATION OF LATTICE MATCHED EPITAXIAL GROWTH OF CUBIC GALLIUM NITRIDE ON BORON PHOSPHIDE

The development of cubic gallium nitride is impeded by the lack of suitable substrate material for lattice-matched epitaxy. This paper presents an explorative investigation into the lattice matched epitaxy of cubic GaN on cubic boron phosphide. The lattice parameter of cubic BP is only 0.4 % larger than that of GaN, and therefore a possible candidate. Monocrystalline BP substrates can be obtained by depositing a thin film epitaxially on Si(100) wafers. The compound semiconductor consists of elements which are readily available in Si semiconductor manufacturing processes. Two sequences have been investigated: consecutive growth of BP and GaN on Si(100) substrates, and growth of GaN on previously prepared epitaxial films of BP on Si(100). The first sequence results in the formation of epitaxial GaP, due to the residual phosphorus in the CVD system. The second route fails at high temperatures due to the decomposition of BP. Large hexagonal GaN crystals, as well as a gallium containing amorphous phase, are formed directly on the silicon wafer. At lower temperatures, hexagonal GaN is formed on the BP surface.
Synthesis and optoelectronical characterization of boron phosphide
7.1 Introduction
In the past decade, interest in the nitride compound semiconductors GaN and AIN has increased tremendously [1]. This is driven by their excellent electron and hole transport properties in combination with a wide bandgap, enabling the fabrication of devices that can be driven at high frequencies and voltages. In addition, the excellent miscibility of the system Ga-Al-In-N provides a large window for bandgap engineering. This strongly extends the possibilities for wide-bandgap devices [2]. GaN has received most attention, because it can be used in light emitting devices in the blue and UV spectral region [3]. GaN growth experiments, as well as literature on this material, show a strong inclination towards the wurtzite lattice (a = 3.189 Å, c = 5.185 Å), at the expense of the zinc-blende structure (a = 4.52 Å). However, due to the higher order of symmetry, the latter is expected to show the better transport properties. The main hindrance in the development of device quality cubic (and in lesser extend, hexagonal) GaN is the lack of suitable substrates, providing the necessary footprint for the correct atomic arrangement. Recent literature on the synthesis of cubic GaN reports the use of GaAs, GaP, β-SiC, and Si [4]. To accommodate the lattice mismatch of the latter, often an intermediate layer is used [5]. Successful synthesis is found to be strongly limited by the lattice mismatch and surface chemistry of the substrate. All systems are restricted to a narrow range of temperature and gas composition. There is, however, a candidate for lattice-matched cubic epitaxy, namely cubic boron phosphide (BP). This compound semiconductor has a lattice parameter of 4.53 Å, and epitaxial growth on silicon has been reported by several groups [6-9]. Boron phosphide has outstanding mechanical and chemical properties: Takigawa reports a Micro-Vickers hardness number of 4700 kg/mm² [10], whereas the only known etchants for BP are fused alkalis at 400-500 °C [11]. The material has been investigated for use as optical window for liquid junction silicon solar cells [12]. The present investigation concerns the use of a BP intermediate layer on silicon for epitaxial growth of cubic GaN. It is well known that cubic BP grown epitaxially on silicon exhibits the effects of strain induced defects. However, the temperature range of synthesis of cubic BP [13] is much broader than that of cubic GaN, because the formation of wurtzite material is not observed in the BP system. Regarding the relatively small research effort put into the development of epitaxial BP, improvement can be expected, especially if BP is suitable as substrate for epitaxial growth of cubic GaN. In this paper, we present the first
Table 7-I. Schematic representation of the two synthesis routes that were investigated for the growth of Si/BP/GaN (100) structures.

<table>
<thead>
<tr>
<th>Substrate cleaning</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition of BP(100)</td>
<td></td>
</tr>
<tr>
<td>( T_{\text{subs}} )</td>
<td>930° C</td>
</tr>
<tr>
<td>( p(\text{BBBr}_3) )</td>
<td>0.3 Torr</td>
</tr>
<tr>
<td>( p(\text{PBr}_3) )</td>
<td>3 Torr</td>
</tr>
<tr>
<td>Total flow</td>
<td>1800 ml/min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cool down to approx. 700° C</th>
<th>Cool down to room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repetitive purging of reactor</td>
<td>Reactor cleaning</td>
</tr>
<tr>
<td>Introduction of NH(_3)</td>
<td>Substrate cleaning</td>
</tr>
<tr>
<td>Deposition of GaN</td>
<td>Deposition of GaN</td>
</tr>
<tr>
<td>( T_{\text{subs}} )</td>
<td>850° - 950° C</td>
</tr>
<tr>
<td>( p(\text{TMG}) )</td>
<td>3-30 Torr</td>
</tr>
<tr>
<td>( p(\text{NH}_3) )</td>
<td>370 Torr</td>
</tr>
<tr>
<td>3250 ml/min</td>
<td>3250 ml/min</td>
</tr>
</tbody>
</table>

results of our investigations to achieve the cubic heterostructures consisting of a Si(100) substrate, a BP(100) intermediate layer, and a GaN(100) top layer.

### 7.2 Experimental

Two deposition procedures were followed: consecutive deposition of BP and GaN on Si(100) substrates, and deposition of GaN on Si(100) and Si/BP(100) substrates (a schematic sequence is presented in Table 7-I). Both materials were grown by thermal chemical vapour deposition, using reduction of BBBr\(_3\) and PBr\(_3\) in hydrogen and decomposition of trimethylgallium (TMG) and ammonia, respectively. The first three precursors are liquids, and were supplied by saturation of hydrogen carrier gas by means of bubblers and reflux coolers. The precursor fluxes were controlled by the temperature of these coolers, and by the supply of the carrier gas. The appropriate gases were mixed and diluted in hydrogen, and fed into a vertical cold wall CVD reactor, which was kept at atmospheric pressure for both depositions. Different flow rates and precursor ratios were used within the range given in Table 7-I.

Pieces of 25-100 mm\(^2\) Si (100) were ultrasonically cleaned in acetone, water, and subsequently oxidized by HNO\(_3\). After stripping the oxide layer in a HF-dip, followed by a rinse in isopropanol vapour, they were placed on a graphite substrate holder. The Si/BP substrates were ultrasonically cleaned in acetone and water, and dried with isopropanol vapour. The surface temperature of the holder and the substrate was monitored by an optical
pyrometer. Temperature fluctuations over the surface were found to be smaller than 3°C. Special care was taken to avoid the formation of ammonium bromide by introducing the ammonia into the reactor directly at the reaction zone via a separate inlet.

For the experiments in which the layers were grown consecutively, the procedure was as follows. The film of epitaxial BP was formed at 950°C from a mixture of BBr₃ and PBr₃ diluted in H₂. After a thickness of 200 nm was reached, the precursor flows were switched off. The reaction chamber, as well as the NH₃ supply line, was purged by repetitive pumping and filling with hydrogen. To prevent a rise in temperature on the susceptor during the pumping, the RF power was reduced. After this purge, the hydrogen flow was restored at atmospheric pressure, and the RF power was increased to obtain a substrate temperature of 950°C. Then, a flow of NH₃ was switched on, followed by the addition of trimethylgallium to the hydrogen carrier. After one or two hours, the precursor gases were switched off, followed by the RF current. Under a small H₂ flow the substrate and holder were cooled down to room temperature.

For the second series of experiments, both bare Si wafer material and previously prepared Si/BP structures were used in the reactor. Deposition took place after the substrates were heated to 850°C-1000°C under hydrogen at atmospheric pressure, following the previous procedure after the purging step.

The crystallinity of the structures obtained was inspected by X-ray and electron diffraction (using a Philips PW4045 powder diffractometer, and a Philips CM30T high resolution TEM). The Si(400) super-reflection was used to ascertain the correct orientation of the sample with respect to the X-ray source and detector. To avoid damage to the detector, the scan was restricted to angles smaller than the strong silicon peak at 72° 2θ. The morphology was analysed by electron microscopy (JEOL EM25 scanning electron microscope, and the above-mentioned high resolution TEM). Both microscopes were equipped with energy dispersive X-ray (EDX) analyser (using ISIS/LINK acquisition software) with a detection range down to boron. However, quantitative analysis was found unreliable due to the inhomogeneous nature of the deposits (thin films, grains, and whiskers), combined with the low sensitivity for the light elements.
Figure 7-1. X-ray diffraction spectra of three typical deposits on Si(100), after the consecutive BP and GaN growth procedures. The sample is oriented to obtain the Si(400) reflection (which is omitted to prevent detector damage). As a reference, the spectrum of the SiO2 sample holder is also depicted.

7.3 Results

The first series of experiments, consecutive depositions of BP and GaN, yields a gold-coloured thin film with a rough appearance. SEM analysis show a top layer consisting of grains of typically 2 micrometer in diameter. EDX spectra reveal the presence of boron, phosphorus, silicon, nitrogen and gallium. X-ray diffraction spectra of three typical deposits are shown in Figure 7-1. As a reference, the spectrum of the glass sample holder is also shown. Two spectra show peaks at 39 and 62 degrees 2θ, which can be attributed to the (200) and (22-1) reflections of a cubic lattice with a = 4.54 Å [14]. The (22-1) peak is caused by twinning, which is generally observed for epitaxial BP on Si(100). Transmission electron microscope analysis reveals that the deposit on silicon wafer consists of a film of BP(100) and small crystalline islands (Figure 7-2) with a {1 1 1} separation of 3.148 Å. Although these
islands are often separated by an apparently amorphous buffer layer, their orientation is aligned with the BP film and the silicon substrate. On the graphite susceptor, a layer of transparent wurtzite GaN crystals, sizing up to one mm. in diameter, is obtained.

The second series of experiments yields in depositions that differ from the first series. Depositions on Si(100) and Si/BP(100) substrates at low temperature consist of hexagonal platelets (Figure 7-3), perpendicular to the surface. On Si/BP substrates few large grains with typical diameter of 5-6 micrometer are found. Increasing substrate temperature to 1000°C results in grains of several micrometer in diameter on the bare silicon substrates, whereas on the Si/BP the deposit consists of whiskers. During several of these high temperature runs the BP film has disappeared.

7.4 Discussion

X-ray diffraction spectra of these kind of thin film structures, obtained a by powder diffractometer, should be interpreted with caution, especially if lattice deformation is expected. However, they are useful for a first inspection in addition to SEM images. Apart from the BP reflections, sample 21 shows peaks at 33°, 48° and 57°, which can be attributed to reflections by (100), (102) and (110) of hexagonal GaN. The intensity of the BP(22-1) reflection is much stronger (relative to (200)) compared to BP/Si substrates prior to the GaN synthesis step. We attribute this to the decomposition of the BP layer during exposure to the reducing atmosphere[15]. The features in the spectrum of sample 23 between 30 and 35° 2-θ suggest a GaN(100) reflection broadened by lack of long range order.

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The results show that gallium forms a compound with phosphorus, rather than with nitrogen. The source of this phosphorus originates from the preceding synthesis of cubic BP. In this deposition an overpressure of phosphorus is needed to prevent the formation of amorphous, boron rich B₃P [13]. The overpressure leads to the formation of solid P₂ on the cooled walls and alumina pedestal. Due to the reducing power of hydrogen and the relatively high vapour pressure of phosphorus, the formation of GaP can not be prevented, even after a NH₃ pre-treatment of the BP film prior to the introduction of the TMG.

Although the origin of these whiskers has not been determined, often a catalyst is responsible for the initiation of whisker growth [16]. We recently reported on the vapour-liquid-solid mechanism in the BB₃-PBr₃-H₂ CVD system [17]. This can be either a contaminant, present on or buried in the substrate surface, or one of the elements of the materials of the structure. The most likely cause for whisker formation is the existence of metallic gallium on the substrate surface. Although its melting point is even below room temperature, at 900 °C the Ga vapour pressure is only 0.7 mTorr [18]. This whisker forming mechanism can possibly be prevented by reducing the (Ga) precursor flow rate.

7.5 Summary and Conclusions

The growth of cubic GaN / BP heterostructures on Si(100) substrates has been investigated. In this heterostructure, BP acts as an intermediate layer to enable the transition from the relatively large silicon lattice to the small lattice of cubic gallium nitride. BP consists of elements readily available in silicon semiconductor processes, and silicon wafers provided with a thin epitaxial film of BP could be manufactured within the existing resources.
Experiments show that the main difficulty for both routes is phosphorus contamination. Consecutive growth of BP and GaN results in growth of GaP in stead of GaN. After the epitaxial growth of BP, phosphorus is abound in the reaction chamber. The orientation of the GaP is determined by the epitaxial Si/BP structure. The growth of GaN on Si/BP structures in a clean (or second) chamber resulted in hexagonal GaN grains at relatively low temperatures, whereas at higher temperatures, whiskers are formed. Results suggest a low temperature seeding-layer has to be applied, followed by a high temperature cubic GaN growth. Alternatively, a different gas system producing cubic GaN at lower temperatures.
References

14 Schroten, E., A. Goossens, and J. Schoonman, to be published.
Chapter 8

SUMMARY
Synthesis and optoelectronic characterization of boron phosphide
This thesis is the result of a study into boron phosphide, a semiconductor material that is not, and will never be, one of the favorites for the semiconductor industry. However, especially these rather unknown materials are great challenges to material scientists working in academic laboratories. Working with them confronts the researcher with the fact that material science heavily relies on a cumulative research effort. In spite of the availability of modern material analysis tools, lack of data, for example for calibration, strongly limits the ease of interpretation of experimental results. If results are obtained, this will both broaden the basis of semiconductor models, on which new ideas grow, as well as provide chances to enlarge the window (e.g. temperature range, selective sensitivity, chemical resistivity) of applications for semiconductor devices.

Taking up the study of such a material does not start with a very concrete question. The researcher can and has to choose the particular points of focus. In this study, the focus has deliberately been spread out into three areas: synthesis, properties, and device application. In each area, two studies were carried out, producing many opportunities for future interest.

This thesis starts with an overview of the material properties and the recipes of successful synthesis routes available in literature. The chemical vapor deposition technique was chosen as the most reliable, regarding contamination, and versatile in view control over process parameters. The particular synthesis system, a cold-wall reactor using the reactants borium bromide and phosphor bromide in a hydrogen atmosphere, was described in chapter 2. The synthesis products were in accordance with the CVD-diagram for the bromide system constructed by dr. Kelder. The control over reaction parameters provides the means of choosing the material properties of the product within a considerable range.

The versatility of chemical vapor deposition was illustrated by the synthesis of highly porous boron phosphide, described in chapter 3. This peculiar surface morphology is very useful for exploiting or adjusting the material properties. Adding seeding material to the substrate forms nucleation spots for the growth of needles of crystalline BP. Films exhibit a very large surface area whilst retaining the electronic properties of crystalline material. Because this is a highly desired property for use in liquid junction solar cells, a later chapter (6) was devoted to this application.

In chapter 4, the results of BP epitaxy on Si were presented, dealing with the large lattice mismatch of this system. Exposure of the silicon substrate to phosphorus in a hydrogen atmosphere at elevated temperatures was found to have a strong roughening effect on the
Si/BP interface. To achieve flat interfaces, this has to be suppressed. This requires a rapid introduction of the reaction species as soon as the synthesis temperature is reached. In addition, it was shown that addition of Si into the BP lattice induces the change of the preferred conductivity type from n-type to p-type. Obtaining Si doping levels that are sufficient to change the conductivity type requires a relatively high precursor content in the reaction mixture. The deposition parameters used in these experiments were close to the limit of the cubic BP phase.

In chapter 5 the results of a study into the fundamental properties of cubic boron phosphide were reported. Using the modulation spectroscopy techniques electro reflectance and photo reflectance, the fundamental band to band transitions of cubic boron phosphide had been determined. Most knowledge of III-V semiconductors is based on the study of GaAs. During the last decade, more elements were put into the database: Indium and phosphorus are added to GaAs, thereby obtaining a means of tuning the optical bandgap, and the nitrides have emerged, especially GaN. However, only if different materials are studied, a distinction can be made between general III-V semiconductor properties and properties peculiar to specific compounds or sub-groups, such as GaAs, arsenides, or ionic III-V compounds. Due to the covalent character of the B-P bonds in cubic BP, the influence of the ionicity of bonds on the electronic properties could be addressed in a comparative study of BP and more ionic III-V compounds.

The practical use of BP cannot be absent in this thesis of applied science. Because of the limited data on the material, only few applications have been proposed, even fewer have been investigated. Here, the investigation of two applications in different fields are presented. In chapter 6, an inorganic version of the well-known Grätzel-type solar cell was proposed, synthesized, and studied. Thin film solar cells all suffer from the fact that strong light absorbing materials are poor electric conductors. Prof. Grätzel proposed to use two different materials for these functions, a sensitizer and a semiconductor. By using porous semiconducting materials, the sensitizer can be made extremely thin without reducing light absorption in the complete cell. The porous BP film synthesized by a vapor-liquid-solid CVD mechanism, described in depth in chapter 3, is combined with the strong absorbing amorphous B$_3$P. The entire structure was fabricated in one single chemical vapor deposition system: The porous structure formed due to the addition of seeding material onto the substrate. Once the structure was formed, a change in the supply of one of the precursors, resulted in the deposition of the sensitizer. The absorption characteristics of this sensitizer, amorphous boron
phosphide, can be optimized: the bandgap is a function of the precursor contents and layer thickness is simply determined by the product of deposition rate and time. Although the efficiency was low, the response of the cell was broadened substantially by the sensitizer, covering most part of the visible light spectrum.

The second application was described in chapter 7, an intermediate layer for the synthesis of epitaxial layers of GaN on Si substrates. Epitaxy on silicon is very desirable for applications of other semiconducting material, because of the maturity and low price of the silicon semiconductor industry. Boron phosphide consists of two elements that are already applied as dopants in the silicon factories. By using BP as an intermediate, no new elements, that can introduce new sources of contamination, are introduced in the process. BP covered silicon wafers could be the ideal substrate material for GaN epitaxy. GaN is a relatively mature compound, which cubic form has a lattice parameter that exactly matches that of BP. Within the synthesis window of our chemical vapor deposition system, we did not succeed in the synthesis of the proposed structure starting from bare silicon wafer material. GaP was formed on the Si/BP, caused by the abundant presence of phosphorus species in the reactor after the BP synthesis. GaN should be deposited onto a Si/BP substrate in a separate process. It was shown that even then, process parameters should be mild: at reaction temperatures above 850 °C in reducing circumstances, phosphorus from the BP will contaminate the process.

These studies clearly show that boron phosphide could play a role in many different areas, varying from semiconductor theory to solar cells. Main hindrances are the lack of data and the availability, main advantages are the compatibility with crystalline silicon and the discoveries to be made.
Chapter 9

SAMENVATTING
Dit proefschrift is het resultaat van een onderzoek naar boriumfosfide, een halfgeleidermateriaal dat geen hoge ogen gooit in de halfgeleiderindustrie, en dat ook nooit zal gaan doen. Toch zijn juist dit soort betrekkelijk onbekende materialen erg interessant voor onderzoekers in academische laboratoria. Als de onderzoeker zich erin verliez, voelt deze aan den lijve dat toegepaste materiaalkunde sterk afhankelijk is van een opeenstapeling van onderzoeksresultaten. Ondanks de beschikbaarheid van moderne analytische technieken, blijken deze maar beperkt bruikbaar als er niet al een hoeveelheid gegevens over het betreffende materiaal bekend is, bijvoorbeeld voor calibratie. Maar als onderzoek resultaat oplevert, kan dit zowel de basis van de modellen voor halfgeleiderfysica verbreden, waardoor nieuwe ideeën ontstaan, als ook het toepassingsgebied van halfgeleiderelektronica (bijvoorbeeld in temperatuurbereik, selectieve gevoeligheid, chemische resistentie).

De start van een dergelijk onderzoek begint niet met een erg concrete vraag. De onderzoeker kan en moet zelf zijn blik toespitsen. In dit onderzoek is de aandacht op drie verschillende gebieden gericht: synthese, eigenschappen, en toepassingen. Op elk gebied zijn twee deelonderzoeken uitgevoerd, die een scala aan mogelijkheden blootleggen.

Het proefschrift begint met een overzicht van de materiaaleigenschappen en de mogelijke syntheseseroutes, die beschreven zijn in de literatuur. Op grond daarvan is de Chemische Vorming uit Damp als meest geschikte techniek gekozen, vanwege de hoge graad van zuiverheid en de goede controle over de syntheseomstandigheden. In hoofdstuk 2 is het specifieke koudewand-systeem, met als reactanten boriumbromide en fosforbromide in een waterstofomgeving, beschreven. De producten uit dit systeem kwamen overeen met het CVD-diagram dat dr. Kelder eerder publiceerde. Controle over de syntheeomstandigheden geven de mogelijkheid om de materiaaleigenschappen te sturen.

De veelzijdigheid van de CVD-techniek komt goed tot uiting bij de synthese van sterk poreus boriumfosfide, beschreven in hoofdstuk 3. Met deze speciale structuur kunnen de materiaaleigenschappen goed tot hun recht komen, of juist gewijzigd worden. Materiaal aangebracht op het substraat vormt kiemen voor de groei van naaldvormige kristallen. Een laag van dit materiaal heeft een zeer groot specifiek oppervlak, terwijl het toch de goede elektronische eigenschappen van het kristallijne materiaal behoudt. Omdat deze constructie zeer geschikt is voor natte zonnecellen, is hier een later hoofdstuk (6) aan gewijd.

In hoofdstuk 4 worden de resultaten gepresenteerd van het onderzoek naar epitaxiaal BP op Si. Dit systeem wordt gekenmerkt door een groot verschil in de roosterconstante tussen
beide materialen. Er werd gevonden dat fosfor in een waterstofatmosfeer bij hoge temperaturen het substraat sterk verruwt. Om een vlakke overgangslaag tussen BP en Si te krijgen, moet de groei van BP snel op gang komen als de synthesetemperatuur is bereikt. Verder werd vastgesteld, dat het inbouwen van Si in het BP rooster de effectieve geleiding van n-type naar p-type verandert. Om daadwerkelijk een omslag in het geleidingstype te verkrijgen, is een relatief hoge concentratie doteringsgas nodig. De syntheseomstandigheden komen hierdoor in dit systeem dicht aan de rand van de kubische kristallijne fase te liggen.

In hoofdstuk 5 worden de resultaten gepresenteerd van een onderzoek naar één van de fundamentele eigenschappen van kubisch boriumfosfide. Met behulp van gemoduleerde electro-reflectie and foto-reflectie is de fundamentele overgangsenergie bepaald. De meeste kennis over III-V-halfgeleiders is gebaseerd op onderzoek naar GaAs. In de laatste jaren is daar resultaten van onderzoek naar andere leden van deze groep aan toegevoegd: GaAs vermengd met indium en fosfor, waarmee de grootte van de optische bandgap aangepast kan worden, en de nitrides, vooral GaN. Echter, alleen als er gegevens van verschillende materialen bestudeerd worden, kan er onderscheid worden gemaakt tussen algemene III-V eigenschappen en eigenschappen die specifiek gelden voor subgroepen als GaAs, arsenides, of ionogene III-V verbindingen. Omdat de B-P binding in kubisch BP nagenoeg covalent is, is BP zeer geschikt om de invloed van het ionogene karakter van halfgeleiders te onderzoeken.

Praktische toepassingen kunnen niet afwezig blijven in een proefschrift op het gebied van de toegepaste natuurwetenschappen. Omdat er weinig gegevens over BP bekend zijn, zijn ook maar weinig toepassingen voorgesteld, en nog minder onderzocht. Hier zijn twee toepassingen, op verschillend terrein, onderzocht. In hoofdstuk 6 is een anorganische variant op de bekende Grätzel-type zonnecel voorgesteld. Deze is uitgewerkt met de resultaten van de synthese en karakterisatie van dergelijke constructies. Dunne-film zonnecellen gaan gebukt onder de slechte elektrische eigenschappen van materialen die licht goed absorberen. Prof. Grätzel stelde voor om voor deze functies twee materialen te gebruiken, een sensitizer en een halfgeleider. Door poreus halfgeleidend materiaal als drager te gebruiken, kan de absorberende laag extreem dun gemaakt worden zonder dat de absorberende eigenschappen van de gehele cel slechter worden. De in hoofdstuk 3 beschreven poreuze BP film verkregen door het vapor-liquid-solid CVD mechanisme, werd gecombineerd met het sterk licht absorberende amorf B₄P. De gehele structuur is in dezelfde CVD opstelling gemaakt: het poreuze kristal door toevoeging van kiemen aan het substraat. Zodra deze structuur was verkregen, werd de toevoer van één van de reactiegassen zodanig gewijzigd, dat een amorf
laagje zich af ging zetten op de naalden. De optische bandgap wordt bepaald door de gassamenstelling gedurende de synthese en de dikte van de amorf laag. Door depositionsnelheid en groeitijd kunnen de absorptie-eigenschappen van deze sensitizer, amorf boriumfosfide, worden geoptimaliseerd. Er werd aangetoond, hoewel de opbrengst laag was, de zonnecel over een groter deel van het zichtbare spectrum werkzaam was.

De tweede toepassing, beschreven in hoofdstuk 7, was boriumfosfide als bufferlaag voor epitaxiale groei van GaN op Si. Gebruik van silicium als drager voor epitaxiale structuren is zeer aantrekkelijk vanwege de vooraanstaande positie en prijs van Si. Boriumfosfide bestaat uit de twee elementen die bij Si structuren gebruikt worden voor dotering. Daarom zijn bij de synthese van BP geen nieuwe synthesegassen nodig. Si wafers met een BP laag kunnen het ideale substraat zijn voor kubisch GaN, omdat de roosterconstante van GaN en BP gelijk zijn. Echter, binnen de grenzen van de syntheseomstandigheden van ons CVD-systeem konden wij geen structuur krijgen op kaal Si basismateriaal. Vanwege de ruime aanwezigheid van fosfor in de reactor na de groei van BP werd GaP gevormd. De structuur moet worden gevormd door GaN aan te brengen in een apart proces. Er werd aangetoond dat de procescondities zelfs dan mild moeten zijn, omdat in reducerende omstandigheden bij temperaturen boven 860 °C, de fosfor uit het BP het proces zal verontreinigen.

Deze resultaten tonen duidelijk aan dat boriumfosfide een rol kan spelen in verschillende toepassingsgebieden, variërend van halfgeleidertheorie tot zonnecellen. De belangrijkste beperkingen zijn het gebrek aan gegevens en de beschikbaarheid, de sterke punten zijn de compatibiliteit met kristallijn silicium en de ontdekkingen die gedaan kunnen worden.
Dankwoord.

Eindelijk is de afronding van mijn promotieonderzoek daar. De geschiedenis van dit proefschrift vindt zijn oorsprong in de vier jaren onderzoek aan boriumfosfide, die ik in het Laboratorium voor Anorganische Chemie heb besteed. Ze horen formeel zelfs tot een andere eeuw. Maar een geschiedenis stort zich niet veel aan de getallen in de tijdslijn.

De vier jaren vormen een belangrijke schakel in mijn leven. Daar ben ik er van doordrongen geraakt dat zinvol werk niet alleen gedaan moet worden.

Het experimentele gedeelte van het onderzoek is tot stand gekomen door de als vanzelfsprekende ondersteuning in het Laboratorium, vooral Ben Meester was hierin onmisbaar. Hij draagt de ervaring opgedaan bij de bouw van een reeks CVD-syntheseopstellingen.

De groep promotendi, bijeengebracht door Joop Schoonman, vormde een goede omgeving voor experimenteel CVD-werk. Het precisiewerk heb ik onder de knie gekregen in “ons” electro-optisch lab, waar Albert Goossens iedereen aanzette tot het aftasten van de meetlimieten van de apparatuur. Samen met Gerrit Bosschloo en later Roel van de Krol konden we steeds meer varianten van meetopstellingen toepassen.

Voor de voortgang op wetenschappelijk gebied ben ik veel dank verschuldigd aan mijn co-promotor Albert Goossens. Hij heeft mij de kracht van wetenschappelijk verwoorden laten zien, door de metamorfooses die een eerste opzet voor een publicatie ondergingen voordat ze publicatierij waren. Hoewel mijn promotor Joop Schoonman veel aan Albert overliet, was hij toch op een aantal punten sterk van invloed op mijn werk. Om te beginnen de motivatie om in de groep aan boriumfosfide te werken. Bovendien zijn houding zaken (en mensen) met elkaar in verband te brengen.

Hoewel mijn prioriteiten in de jaren na afloop van het experimentele werk anders zijn komen te liggen, ben ik dankbaar voor de steun en het vertrouwen die noodzakelijk waren voor het afronden van dit werk. Vanuit het Laboratorium, vanuit mijn werkkringen, en vooral vanuit mijn familie, Karel en Peter. Het uitsmeren van een dergelijk proces betekent veel extra werk. Zaken die niet urgent, maar wel belangrijk zijn, komen heel vaak in het gedrang. Meestal worden ze uiteindelijk toch wel urgent... Gelukkig is geduld een essentiële eigenschap voor wetenschappers.