Politechnika Wrocławska
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Recenzja pracy doktorskiej pani mgr. Karolina Żelazna

„Optical properties of novel III-V-N alloys"

Na początku chciałem przeprosić za to, że recenzję napiszę po angielsku. Jednak dla mnie jako Niemca jest naprawdę trudno, napisać po polsku o pracy naukowej napisanej po angielsku ...

The topic of this PhD thesis is very interesting and covers a research area being currently of high interest in the scientific community. Classical semiconductors like Si, Ge, cubic III-V and II-VI compounds have been widely studied concerning their basic properties and application potential. The same is basically true for the group-III nitrides, being widely applied in optoelectronic and recently as well in electronic devices, although some basic physical questions still remain open.

In the introduction a very good comprehensible and at the same time brief motivation is presented. Mgr. Karolina Żelazna studied epitaxial structures based on GaP as host material with a certain amount of nitrogen and arsenic. Those $GaN_yAs_xP_{1-x-y}$ compounds are interesting photonic materials for integration with silicon due to a rather small lattice mismatch between GaP and Si. These studies are well motivated by future applications in intermediate band solar cells, which can use the well developed, Si-based technology. The advantages of such an integration is well discussed on the examples of $GaAs_xP_{1-x}$ and $GaIn_xP_{1-x}$. The intermediate band solar cell (IBSC) concept is introduced and compared to other design approaches of novel solar cells like the multi-junction cell, nanocrystals or quantum dots as active part or hybrid solutions of organic and inorganic materials. Such practical considerations at the introduction of a PhD thesis are a clear evidence for the high motivation of the PhD candidate. Intermediate band solar cells with properly located bands can achieve high conversion efficiencies as explained in fig. 1.8.

The term of highly mismatched alloys (HMAs) is introduced. It is explained on the example of nitrogen replacing a group-V element in classical III-V compounds. Only a limited amount can be introduced and localized electronic states are formed. The Band Anticrossing Model (BAC) is used for explaining the changes in the electronic band structure. It was first developed for diluted nitrides in the group of Prof. W. Walukiewicz, where mgr. K. Żelazna spent part of her PhD time at Berkeley. This model is discussed in detail. The differences in the electronic band structure of GaP and GaAs result in completely different localized states when introducing N to these compounds. This is well illustrated in fig. 1.4 (not fig. 1 as written on page 13). In addition GaAs is a direct semiconductor and GaP an indirect one concerning the band gap. Two approaches of BAC calculations are compared.

To understand the properties of such ternary and quaternary compound semiconductors a variety of spectroscopic techniques were applied. This is introduced in chapter 2. Without going here too much into details it becomes clear why as well absorption-like techniques and emission techniques are needed to come to a better and complex understanding of the studies materials. The basics of electro-modulation spectroscopy are very well explained. For structural characterization as well x-ray diffraction and Rutherford backscattering was used. Summarizing this part of the thesis it can be stated that Karolina Żelazna used a widely spread out arsenal of experimental techniques which is not always common for PhD thesis.

Chapter 3 deals with the sample growth. Although the samples under study were not grown by herself it is impressive how well the molecular beam epitaxy (MBE) as a general method and it modifications are described. It is absolutely right that rf-plasma sources for nitrogen activation and incorporation are the best choice. The crucial growth parameters (plasma stability etc.) are also pointed out well. The growth details of the different sample sets are very well documented. Finally the influence of strain conditions is discussed. Although the substrates used here were GaP wafers (no Si jet ...) strain conditions influence especially the optical data significantly. This is pointed out properly.

In the following chapter the band structure of phosphorous-rich GaNP(As) is discussed. Phosphorous-rich $GaN_xP_yAs_{1-x-y}$ structures with $x \leq 0.25$ and $y > 0.6$ were studied. It is somewhat confusing that the nomenclature of describing the quaternary compounds is not consequent and changed in different chapters ($GaN_yAs_xP_{1-x-y}$ in the introduction, page 9, and $GaN_xP_yAs_{1-x-y}$ chapter 4, page 48). The same is true for the section in the summary, where a "N content of 0.5 – 2.5% and As ≤ 40" is mentioned. All discussed findings are well documented by experimental data based on the mentioned variety of optical methods. Somewhat surprising for me was the second section on page 48 summarizing the results given later on. I would have expected that at the end of this chapter. Sometimes the division between the pages (figures – text) are not done carefully (f.e. pages 51-53) being not helpful for the reader. But in summary the experimental results are highly consistent with the theoretical modeling and overall convincing.

Chapter 5 deals with doped layers being of crucial importance for later practical applications. $GaN_xP_yAs_{1-x-y}$ alloys with a few % N and around 40% P have been identified in the last years as being most promising for IBSC-applications. In this case the nitrogen level is close to the conduction band (CB) minimum of the GaP_yAs_{1-y} host. As illustrated in fig. 5.1 (a) an effective gap between IB and CB is formed suppressing carrier thermalization. In general the energy distances between CB, IB and VB are optimal from solar energy spectrum point of view. To shift the Fermi level toward IB this should be slightly donor doped. This has been studied here based on the available grown MBE-structures. The Si-doping result in a stronger band bending and finally to stronger surface electrical fields and PR signals. Consequences are discussed carefully. The doping concentration has a strong influence as well on intensities and signal broadening. It is therefore concluded that the surface band bending due to the strong electric fields is a key material feature important for applications.

In the next chapter the temperature dependence of the band gap energy is investigated. Transmission and reflection measurements were performed to determine the T-dependent absorption. Data are again very carefully taken and discussed. It turns out that for the intermediate gap semiconductor GaNP(As) a clear reduction in the thermally induced bang gap shift is observed. This reduced temperature sensitivity could provide important input for designing solar energy harvesting of such materials. Whether this is indeed a hint for advantage laser diode applications, as stated in the summary (page 100), is not clear, because many other parameters will determine a laser diode ...

In the final chapter 7 the results of photoluminescence measurements are presented and summarized. Final interpretations are here hampered by the fact that the composition over the grown samples is not homogeneous enough and defects play a role as well. This provides to special potential fluctuations. The carrier localization effects are discussed in detail.

Summarizing this is a really great dissertation and mgr. Karolina Żelazna demonstrated her wide knowledge in experimental optical methods to characterize novel and complicated quaternary semiconductor structures. In addition she has also a good understanding of possible future applications f.e. in intermediate band gap solar cells. The obtained results are well documented and interpreted. I will not point them out all here now in detail. Most important for me was the finding that the incorporation of even a few percent of nitrogen into P-rich GaPAs changes the band gap from indirect to direct due to the formation of an intermediate band. This could be interpreted by the BAC model. Mgr. Karolina Żelazna without any doubts deserve the PhD title for this thesis.

For an experimentalist Mrs. Żelazna has an unusual good understanding of the theoretical background and is able to apply and to interpret results of the BAC model calculations. It is obviously a great benefit that one of the supervisors is a very good experimentalist and the other one of the leading in his field theoreticians. One could imagine more of such 'cross sectional' thesis being of benefit as well from the practical and the theoretical point of view.

There is only one small critical remark at the end: Whereas the introduction is really fantastic, the summary remains somewhat 'unfinished'. At the beginning possible applications were mentioned but at the end a tiny "offers a potential of using P-rich GaNPAs alloys". Here I would have expected some stronger predictions from the PhD candidate based on the presented findings. In contrast to that the final sentence underlines the importance of basic physical studies by stating: "The emission properties … studied intensively … is important to find the optimal parameters in the case of optical applications." I would finally not overestimate the minor critics concerning layout and labeling.

The PhD thesis fulfill all requirements and I am stating that the are

Very good (5.0)

About 'Excellence' the commission should decide based on all circumstances.

Prof, dr. hab. Detlef Hommel

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