MECHANICAL ENGINEERING PHD SCHOOL

HIGH EFFICIENCY SEMICONDUCTOR BASED SOLAR CELLS

Thesis of PhD Dissertation

by

István Réti

Gödöllő, Hungary

2015

Doctoral school denomination:	Mechanical Engineering PhD School
Science:	Energetics of Agricultural and Environmental Engineering
Leader:	Prof. Dr. István Farkas Dr. of Technical Sciences Faculty of Mechanical Engineering Szent István University, Gödöllő, Hungary
Supervisor:	Prof. Dr. István Farkas Dr. of Technical Sciences Institute for Environmental Engineering Systems Faculty of Mechanical Engineering Szent István University, Gödöllő, Hungary

………………………………………………	……………………………………………
Affirmation of the Doctoral School Leader	Affirmation of supervisor

CONTENTS

LIST OF SYMBOLS

E_{av}: average illuminance value [lux]

E_g: band gap of the material [eV]

E_{max}: maximum illuminance value [lux]

P: actual power of PV module [W]

P_{foto}: photo power [W]

T: temperature [°K]

U: actual voltage of PV module [V]

$U_{ü}$: open circuit voltage [V]

$V(\lambda)$: human eye spectral sensitivity [-]

η: PV module efficiency [%]

LIST OF ABBREVIATIONS

CIS: Copper Indium Selenide ($CuInSe_2$) – Copper Indium Selenide solar technology

CIGS: Copper Indium Gallium Selenide ($CuInGaSe_2$) – Copper Indium Gallium Selenide solar technology

GaAs: Gallium Arsenide

InGaAs: Indium Gallium Arsenide

InP: Indium Phosphide

LED: Light-Emitting-Diode

LPE: Liquid Phase Epitaxy

MBE: Molecular Beam Epitaxy

PLC: Programmable Logical Controller

RHEED: Reflection High Energy Electron Diffraction

UHV: Ultra-High Vacuum

ZnO: Zinc Oxide

1. INTRODUCTION AND OBJECTIVES

The gratest challange of today's society is how to tackle evergrowing energy consumption stemming from continuous economic growth.

Apart from the already existing energy transformation solutions, there is a need for state-of-the-art equipment with higher efficiency performance.

One reliable option is to elaborate new heterostructure semiconductors transforming electrical energy directly to light energy and solar radiation into electrical energy more efficiently.

The objectives of my work are as follows：

1. Developing optical classification method, which not only can be classified as a type of a questionable solar panel, but also can be improved the efficiency of the compound semiconductor solar cell by testing with it each intermediate productsphase of the manufacturing process and compare them to the theoretical calculation, thereby providing direction data for the more efficient production.
2. Developing a method, where several specific LED semiconductor creates the basis for the transformation of energy in wide spectrum province and serves then as a basis for high efficiency detectors and solar cells to.
3. Developing a method, using power conversion working in wide spectral rage and developed from special LED semiconductors that helps the production of a semiconductor device that works also as a detector, which energy conversion takes place almost evenly under high efficiency and wide wavelength range.
4. Developing a process, which helps to create a special detector that can determine the current efficiency of any solar cell and improve the homogenity of solar simulators through the exact imitation of the sensitivity of human eye.
5. Setting up a system type model for developing an optimized, new type of semiconductor. Consequently, based on simulations, developing a process, which helps to evaporate new type of solar cell samples with high reliability not only in laboratory conditions, but also in industrial environment.
6. Creating a new, computer-controlled aperture regulation algorithm for the orifice shutter of evaporation sources (Knudsen effusion cells), whereby the number of molecules for experimental samples are controllable.

Through the abovementioned tasks as well as the findings concerning the production of the new semiconductor, I want to show directions for the feasibility of the advanced engineering tasks.

2. MATERIAL AND METHODS

In this section the tools and methods are presented that helped me to solve the above tasks. I have arrived at developing the new high efficiency semiconductor based solar cell via high efficiency heterostructure light emitting devices.

2.1. Liquid Phase Epitaxy

The most common of the epitaxy methods is the liquid phase epitaxy, if the target is a fast and cost-efficient development and production of a less complex hetero structure. Cost-saving is increased if the monocrystal substrate, which can be bought in the trade market, is the basis of the planned layer construction. The aim will be the achieved faster, if the planned semiconductor material system has nearly the same lattice constant as the substrate.

The growth of the semiconductor samples – which the test was performed – was done by, during the liquid phase epitaxy, on the crystalline substrate the single crystal layer was separated from impregnated melt at high temperature (InGaAsP ~ 600°C).
The thickness of the active layer and thereby the operating wavelength become tunable by moving with great attention the heating stove along the reactor tube.

The main aim of my work is the tuning options, in the implementation with semiconductors for broadband energy transformation.

2.2. Molecular Beam Epitaxy equipment

An important condition of creating the GaAs-based solar cell structure is the controlled growth of semiconductor crystal layers and nanostructures. These few atomicscale thick layers and other nanoscale objects can be primarily grown with molecular beam epitaxy due to the following advantages:

- Low deposition temperature does not create imperfections.
- This procedure reduces diffusion between the layers.
- The layers can grow well-controlled, in low speed (0.1-1 atomic row/s) and can be stopped at any time during the process.
- The composition and doping of the material can be well variated by varying the temperature of the Knudsen-cell.
- The superlattices can be very precisely prepared with it.
- Two-, one- and zero-dimensional nanostructures can be prepared without expensive lithography process.

The MBE equipments are build nowadays in horizontal layout according to the orientation of the layer growth. However spread in the use of the sample a complex, but in terms of layer growth a classical vertical form, which has been prioritized on the basis of the experience gained during the privious LED production. It can be seen in Fig. 2.1.

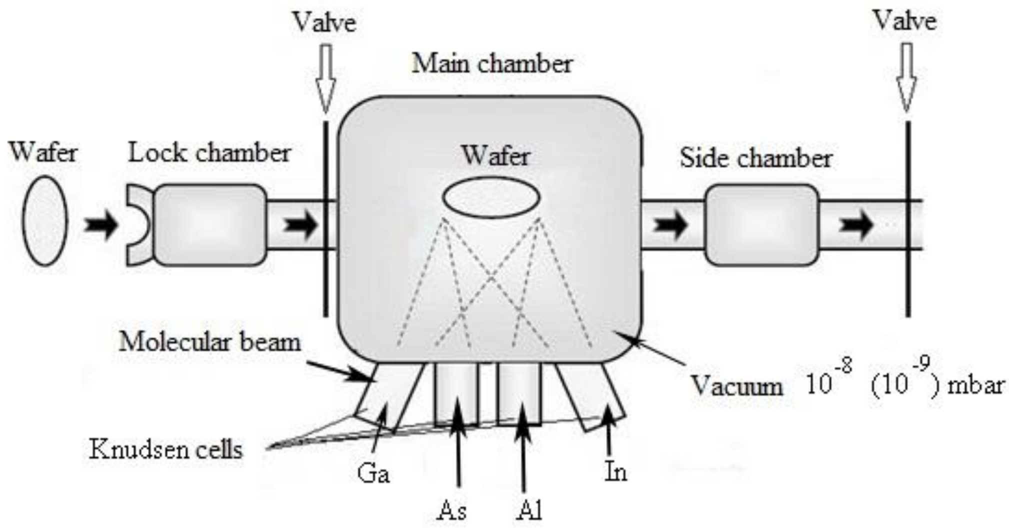

Fig. 2.1. MBE Construction with the vertically performed layer growth

The device can be seen in Fig. 2.1 has 3 main parts:

- Lock chamber for minimalize background impurities associated with moving the experimental semiconductor.
- Main chamber, or reactor chamber, where the layer separation or other structure growth happens, with the help of atomic and molecule beams. These operations are necessary to be carried out under ultra high vacuum (10^{-10} mbar) to have the particles big from path length.
- The side chamber serves mostly to connect multiple vacuum pumps (turbo molecular pump, ion-getter, titanium sublimator).

With the use of the equipment, I have very precisely determined, which hetero-structure should, may or necessary to deal with.

2.3. Fine-mechanic methods of precision movements in ultra-high vacuum

The moving in ultra vacuum space needs many design differences, which has to be significantly different from casual developed solutions in order to maintain the high purity. It is strictly prohibited to use the materials in clean spaces, which sublimable or can carry any impurities.

Because there's a particularly high demand for the UHV by the MBE equipments, therefore one of the major tasks that require causion are the moving of the experimental wafer and its holder.

The tasks solutions are discussed in this chapter.

Movements with small displacement in ultra vacuum

More manufacture are specialized to produce vacuum-tight actuators for basic movements. At the evaporators demanding the clean space, the realization of the multidimensional motions is solved by the combination of mostly these elements. In this case just had to take great care given to assembling the seals.
In some highly complex system, like the MBE, become inevitably the compilation of a special device, which had to be able to implement in case of the sample holder for example movement with five free option.
The feature of this equipment is that merely the semiconductor slice holder hangs down on the end of actuator rod from the viewpoint of UHV into critical space, into the main chamber. The rod is locked with a flexible tube from the outside space for the vacuum density, where the rod can be moved from the outside within the limits set by the tube. Due to the complexity of the task, after the assembly of the finished base elements, remained items that needs special production.
This was a heated molybdenum sample holder. It not only had to observe the heating of the sample to 500 ^{0}C temperature without UHV pollution, but had to keep the mechanical joints with the elements being attached with it, despite the heat motion.

Movements with large displacement in ultra vacuum

Movements with large displacement in the ultra high vacuum - not infrequently comes with one meter distance - happen in many cases not directly, but indirect method. The most widely used indirect method is, which I preferred for its reliability, when a hermetically packaged strong permanent magnet is mounted to the moving device in vacuum, that from the outside it is possible to move it away into the desired directions with the help of an other permanent magnet.

Important criteria for the lock operation of all new wafers, that can not remain any transfer device in the work place, because of the high vacuum requirement. So I had to ensure in the construction of the device a warning system, that specifically pay attention to monitor it.

2.4. Creating and measuring ultra-high vacuum

In the solution of the task by selecting the pumps, it was important to ensure greater pump out power to the clean room processes in the main chamber, therefore the choice fell on the rotary, turbo and sorption pumps.

Production of ultra high vacuum for MBE systems

Producting ultra high vacuum for MBE systems is a multi stage process. Pre-vacuum is created in the first stage (10^{-4} mbar) which I solved with rotary pump. Since the lubricant of this is oil, a safety valve must ensure that the oil is not drawn into the pump out space in case of power cut. The second level of the high vacuum (10^{-8} - 10^{-10} mbar) was reached with one after rotary pump connected the other turbo pump.

However, at the MBE even this value is not enough, therefore the residual gas is usually bind as the third stage. Titanium sublimation pump - which can be connected to the side chamber - was used to solve this, which basic principle is that the residual gas molecules in the vacuum space are ionized with the help of high voltage (5 kV) and magnetic field (0.1 – 0.3 Tesla), then the accelerated ions remain binding after impact the binders surface. The advantage of this binding process is, that operates from 10^{-4} mbar and can reach the 10^{-11} mbar in the end vacuum.

Ultra high vacuum measurement for MBE systems

Only low-pressure range measuring sensors are used for measuring the pressure in the UHV systems.
They have two main types:

- absolute pressure gauges (vacuum gauges),
- partial pressure gauges (mass spectrometers).

Due to the high complexity of my system it was necessary to integrate both types of sensors.

The operating principle of the absolute pressure gauges also limits its measurement range. I used the heat conduction based Piráni vacuum gauge which detects between 100 mbar and 5×10^{-4} mbar for the control measurement of the pre-vacuum produced by the rotary pump. In the main chamber another vacuum gauge type was needed due to the higher vacuum demand, which was the ionization principle based Penning vacuum gauge with 10^{-12} mbar measuring-limit. As the ionization current the device is proportional to the pressure and this interrelation is linear over several orders of magnitude, so the main chambers' surveillance security is guaranteed for the critical space of the vacuum.

Built the partial pressure gauge into the MBE system was necessary, because the vacuum gauges only measure the total pressure. In many cases, as also in our experimental compilation, it was important to know the partial pressures of the various gas and the residual gas components, so we can calculate with other molecules than the planned. The used quadruple mass spectrometer has separated the given gas ions - during the interaction with the electromagnetic field - on the basis of the mass/charge quotient. During the measure, I was able to examine the mass spectra of the residual gas in the system, thereby the device depicted the relative intensity in the function of the mass/charge or mass/atomic number ratio.

2.5. Measurement layers created by MBE equipment for solar cells

For testing grown layers, as thin layers, by MBE equipment, several methods are known, especially with the introduction of new materials *(Brümmer et. al., 1984)*. To apply all of these methods would be wasting, so in this case I selected those, which I could use to my work in MTA-MFA.

Ellipsometry

The ellipsometry is a high sensitive examination in a non-destructive optical principle with which I was able to qualify - also in ultra vacuum - primarily wafer surfaces and thin layer structures. I was able to define the thickness, grain structure and quality of the boundary of the thin layer on the wafer in that case when the dielectric data was also known. The measurement data served a comforting cheque in the examination of the created ZnO layer, however they are stable background for the control series of the new solar cell experimental layers.

Rutherford Backscattering Spectrometry

During the Rutherford Backscattering Spectrometry (RBS), the bombing of the wafer was with 1-5 MeV accelerated He ions which deflected in the number and energy of their characteristics. I was able to define the type of wafer atoms by detecting the energy of the elastically reflected He ions and the concentration of the ions from the number of the same energy levels. With the changing the He ions' angle of incidence in the samples, I was able to calculate the thickness of the experimented layer, based on the energy loss - which is proportional to the larger travel distance - after the calculation I have compared the calculated values with the measured ones of the ellipsometer.

Scanning Electron Microscopy

The Scanning Electron Microscopy (SEM) was the third test method which helped to decide, even explain the differences when I experienced layer thickness differences in the comparative measurement of the ellipsometer and RBS.
The surface of the test wafer has been through scan with the focused beam of an electron gun. From the multi detector data of the deflected electrons, x-ray beams and from the coordinates of the impacts angles I have got useful - some nm resolution - image from the upper layer's grit the locations and quantities of the contaminants and from the layer's thickness, which is important for me.

2.6. Optical classification of solar cells and solar simulator

While the energy scarcity has raised the supply market of the solar panels in the European Union, the government stiffed the original american regulations to achieve higher quality in production of the solar panels.

Solar simulator with halogen lamps

The original role of the solar simulator is to simulate the radiation from the Sun in artificial conditions. Sun radiation in atmospheric space was measured by WMO, comparing with the radiation of the different temperature black bodies, the 5800 ^{0}K temperature one gave the lowest difference.

Based on my previous measurement experience, such color temperature and spectral characteristics could best be approximated halogen lamps. I had the opportunity to review the approximation - in MTA MFA – by a several small halogen lamp build solar simulator on an illumination plane placed in thick matrix.

This solar simulator was created by the Energy Equipment Testing Service Ltd. originally with Philips 3000 ^{0}K color temperature radiant dichroic lamps. The result was spectacular, when we replaced the Philips lamps to the higher temperature radiant 4700 ^{0}K dichroic lamps.
According to the control-measurement has been eliminated in the inhomogeneity of the two type of halogen lamps cone angle difference with the installation of a small absorption, good diffuser foil.
Improving the quality of the solar simulator for the examination of a 1500 x 750 nm solar panel has led to a well suited solution.
Parallel to the recording of the solar cell parameters, it was also needed to measure its temperature of heat up and the received parameter data must be multiplied by correction factor in accordance with the corresponding temperature range, that measured in an accredited laboratory with reference lighting elements mounted on the solar cell holder.

Solar simulator with xenon lamp

In such laboratories, where testing small surface experimental solar panels are also a purpose, those solar simulators are useful, in which less heat issuing, high intensity xenon light are installed as light sources.
In this case, we must not forget of the prominent peaks in the spectrum of radiation as characteristics of the xenon.

Solar simulator alternatives

A claim has arised in the production of the solar panels for an opportunity of a rapid test, that can be added to the production line to give a good approximating information of each completed panel. Until now, the best solution is the simulator with flash tube. Its spectra gives similar differences as the xenon lamp compared to the real solar radiation, however just for a few thousandths of a second period, which corresponds to the early NASA standards, but not for the today’s European standards.

In the recent years, a more promising alternative appeared on the market, namely from semiconductor diodes. Due the widespread use of the MBE, the manufacturing technology of the blue LED is so refined, that sufficiently white light can be produced with a LED covering by different phosphor mixtures to the human eye. This radiation that has mostly three sharp spectral peaks, however is not sufficient for a good solar simulator. The color mixing experimental radiant has better approximation and promises more possibilities in the perspectives by the development of technology which is already well-tried by the theatrical spotlights, in which the three color LEDs driver circuitry was controlled with RGB signals that are already familiar from the television. In this case, a diffuser was needed to build in for the necessary homogenity, and also a collector lens, which I could only reach the prescribed irradiation on a surface with a diameter of only 10 mm of the available LED elements.

3. RESULTS

I present in this section the results, with which I worked out - starting from the lighting semiconductor energy conversion successes - the manufacturing method of the solar cell type operating in a high efficiency advanced spectral range, which can be made using MBE in a controlled manner in the stages of preparation.

3.1. Optical classification method for solar cell production phases

With my new optical classification method, the transmission of the window with front conductive layer can be measured on one hand even in the pre-construction condition. On the other hand it has an ability to an important evaluation, because it can give an internationally certified, accurate picture of joint spectral sensitivity of the newly formed semiconductor.
The basis of my introduced method is the Cary spectrometer, which I modified for the purpose and expanded with the corresponding technical means.
The essence of the method guarantees the accuracy, that during the measurement cycle, every single value of the measurement points are compared with the measured value of the standard detector, calibrated in the National Measurement Office (see Fig. 3.1).

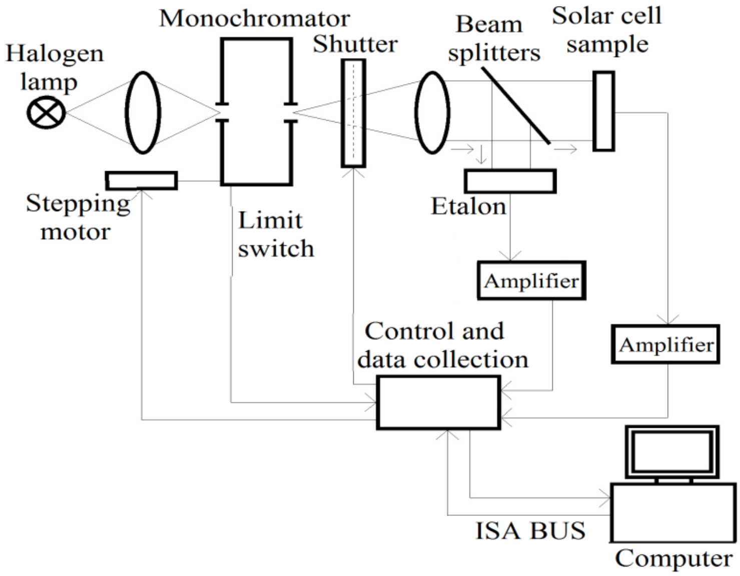

Fig. 3.1. Block diagram of the solar cell sample/model measurement

The light of the halogen lamp is imaged to the entering slit of the spectrometer. The controlled shutter eliminates the darkness current of the detectors after the entering slit. The collimated light beam by the lens is divided into perpendicular directions by a beam splitter: one half of the radiation was directed to the solar cell sample to be tested while the broken direction (5%) was to the standard detector. With the known spectral sensitivity of the standard detector, both the uncertainly arising from the fluctuation in time of the light source and the error from the non-linear wavelength resolution of the monochromator can be eliminated.

After the completion of the controlled measurement cycle, the processing algorithm compares the matrix resulting from the measured values with the reference values, and then draws out the test solar cell sample's spectral curve as seen in Fig. 3.2.

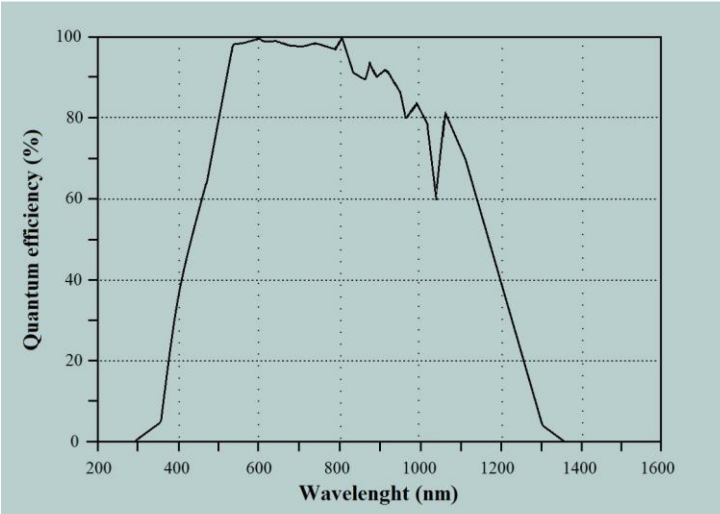

Fig. 3.2. Results of a measurement series

The Fig. 3.3 already shows a measurement setup, where the ZnO front leading layer thickness (w<1 µm) of the CIS solar cell can be clearly optimized before assembling with the help of my method.

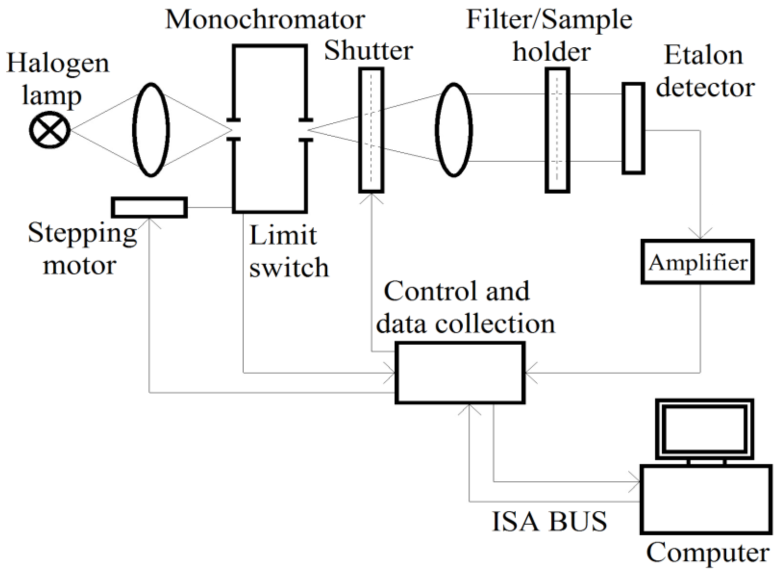

Fig. 3.3. Block diagram of the ZnO sample measurement

The ZnO coating deposited on the glass baseplate functions as an optical filter of the solar panel, so the measuring development of the solar cell sample was modified as follows.

A filter holder was placed to the path of the collimated light beam by the lens – that can get through the shutter – for the layers to be tested, instead of the beam splitter. The known sensitivity characteristic standard accepts the light passing through it. After the completion of the controlled measurement cycle, the processing algorithm compares the matrix resulting from the measured values with the reference values, and then draws out the test sample's spectral curve as seen in Fig. 3.4, from which the solar cell current working phase can be evaluated.

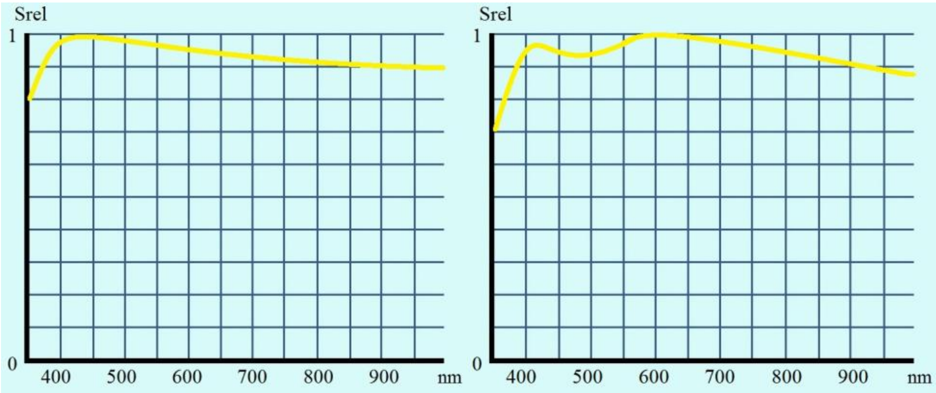

Fig. 3.4. ZnO thickness adjustment phases of the CIS solar cell production

The presented practical results demonstrate, that the yield efficiency of the solar cell production can significantly be increased with the help of the method and serves as a good reference data for the development of new types of solar cells.

3.2. Method for creating wide spectrum diode radiation

The preparation of the multi-wavelength beam LED is assisted by the recognition that - contrary to the clear correlation between the prohibited lane and the grid constant of the ternary materials - the width of the band gap and grid constant can be varied independently in four-component materials (like at the GaInAsP) by altering the ratio of the ingredients.

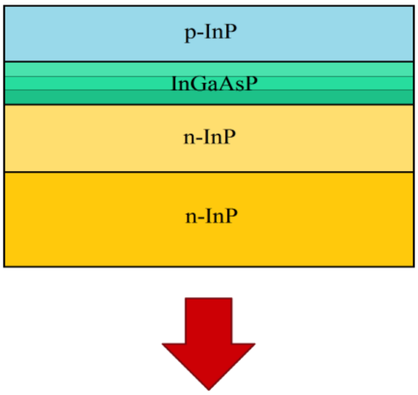

Fig .3.5. Structure of the InGaAsP/InP semiconductor LED

Shown in Fig. 3.5, a same type of InP layer (3-4 µm), then an InGaAs active layer (1-2 µm) and lastly an opposite type of carrier InP layer (6-10 µm) was made to the substrate with a liquid phase epitaxy (LPE) procedure because of its speed and cheapness.

The development of the contact layers were very important. On slice *p* side Au- Zn / Cr / Au, on the other hand, on its *n* side, where the light comes out and therefore I bonded it with a least overshadow 25 µm thick gold wire MECH-EL 907 to a TO 18 socket, the Au-Sn / Au contact layer proved to be the best (see Fig. 3.6).

Fig. 3.6. LED mounted to TO 18 case without epoxy (left) and with epoxy (right)

The right side of Fig. 3.6 shows a LED, which I have covered with transparent epoxy after bonding. The epoxy stabilizes the electrical bond, as well as facilitates the better optical imaging of the light exit from the LED.

The desired wavelength of the radiation from the diodes has been set with the modifying of the active InGaAsP layer composition (see Fig. 3.7).

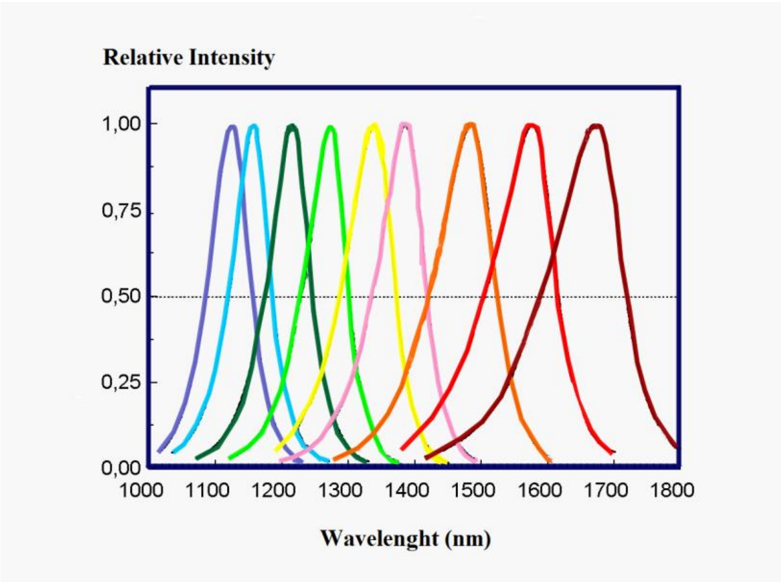

Fig. 3.7. Spectrums of 9 systematically structured InGaAsP/InP LED

I have attempted efficiency enhancements by optical method before the final mounting of the LED series (see Fig. 3.8).

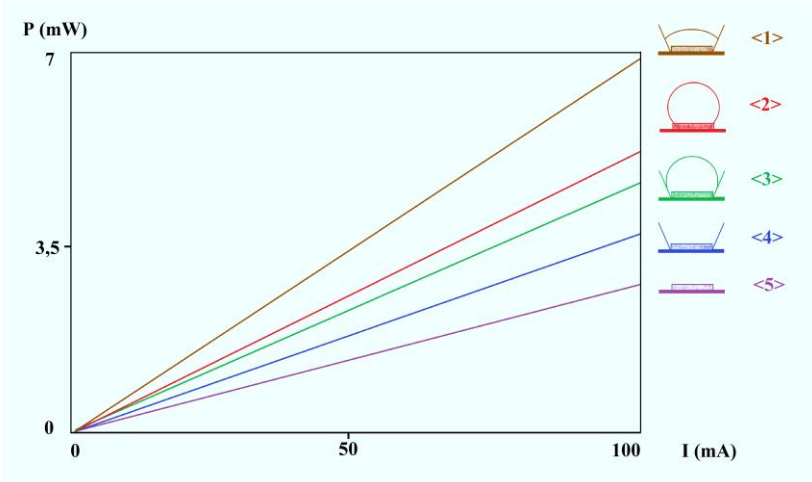

Fig. 3.8 Mirror reflector- epoxy cover combinations impact for extractable power

For the comparisons, I used the small-diameter (50 mm) integrating spherical measurement (as seen on Fig. 3.9) that spread because of its measuring speed *(Martin, Réti et al., 1990)*.

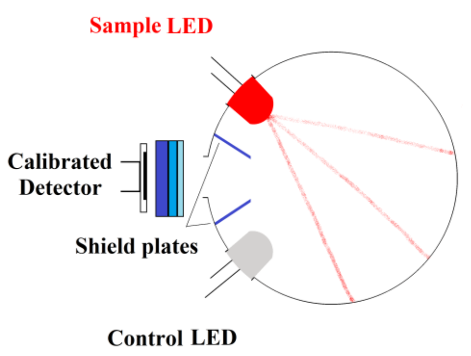

Fig. 3.9. Comparison measurements of mirror reflector- epoxy cover combinations

The measurement errors that derive from the harmful reflections of the small sphere can be eliminated by using the control LED and the calibrated detector together.

I was given a clear indication from the series measurement on how to mount of the LED series - that can also be well used in a spectrometer – for a better lighting.

3.3. Method for widening the spectral sensitivity of InGaAs solar cell

During the method's setup, I used the observation for solid semiconductor energy transfer, which states that a LED structure can be a detector for the same active wavelength range. *(Rakovics et al., 2003)*.
I constructed the method's basis from experiences in a special "LED" detector consisting of several LEDs radiating at different wavelengths and spanning the wide spectrum using modified, four-component, hetero-structure GaInAsP semiconductors operating at 1650 nm wavelength (see Fig. 3.10).

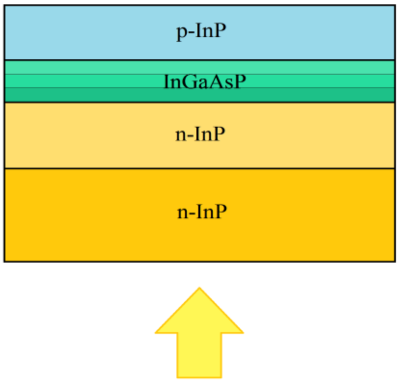

Fig. 3.10. InGaAsP/InP „LED" detector setup

The key to the widened spectrum sensitivity is a three-level InGaAsP active layer. The three active levels' band gap compare to 1150 nm, 1270 nm and 1650 nm wavelength, and serve the purpose of obtaining wider, flatbed spectral sensitivity. The practical problem lies in calculating and creating the width of the three different InGaAsP layers. I was helped by my results with color filter layers (1. thesis), and my experiences during the setup of the LED array active layer (2. thesis).

The first experimental results are promising with the setup working as a low signal to noise ratio, wide spectrum sensitive light converter detector (see Fig. 3.11).

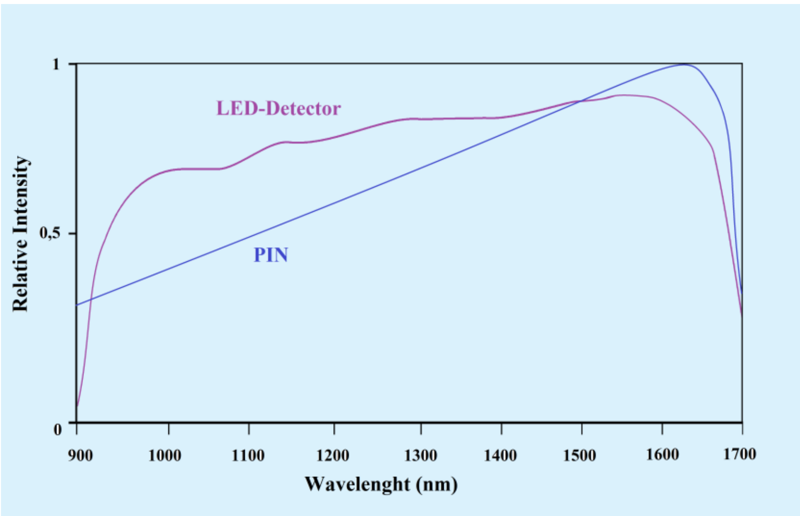

Fig. 3.11. Spectrum of 1650 nm wavelength PIN and „LED" detector

In order to increase the optical efficiency, I measured the different deflection mirror resin combinations for the LED array in the "LED" detector (see Fig. 3.12).

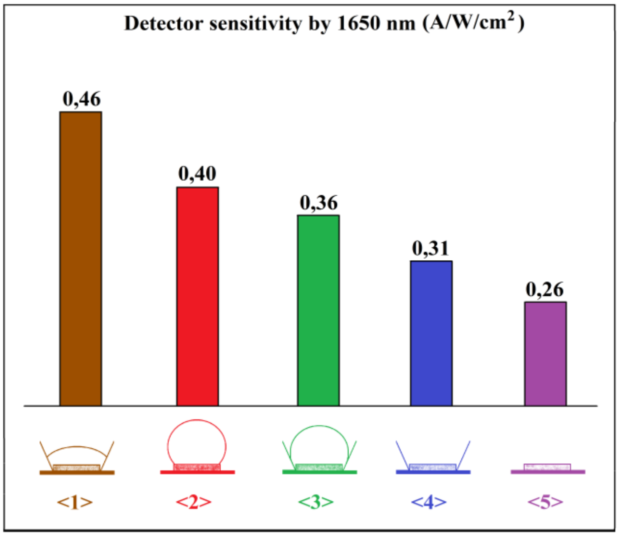

Fig. 3.12. Deflection mirror resin combinations effect on „LED” detectors on 1650 nm wavelength

To measure the deflection mirror resin combination placed in front of the „LED” detector, I used the efficient setup from figure 3.9 with the exception of using my experimental “LED” detector in place of the calibrated filtered detector, and I used the control LED (1215 nm) and sample LED (1386 nm) beams from Fig. 3.7.

The results which help the expansion of LEDs can be transplanted to the field of light conversion as seen from the new “LED” detector system.

3.4. Process to determine the current efficiency of the solar cell

The method in Fig. 3.13 was the result of my optical rating measurements from Fig. 3.1 and Fig. 3.3 used in conjunction with the device created with the optimization program.

Fig. 3.13. Solar module with illuminance meter

The basis of the method is a high-accuracy illuminance meter device created by myself, containing a light detector made from a high-sensitivity silicon which I carefully matched to the human eye's light sensitivity V(λ) curve. After the certification of the measurement device in the National Measurement Office, its accuracy complies with American standards.
The methodological advantage of the standard device is gained because the measuring head's spatial sensitivity is proportional to the cosine of the entering light beam, as can be seen in Fig. 3.14, just like the transformation efficiency of most of the solar panels.

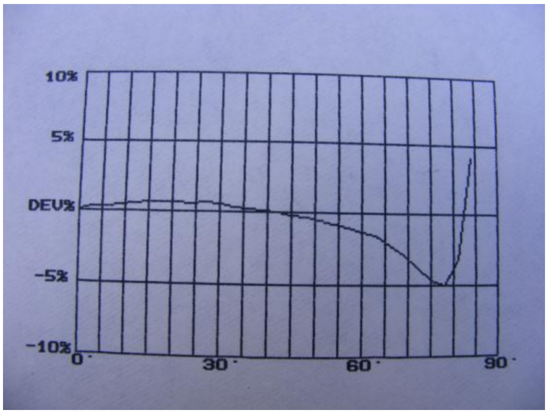

Fig. 3.14. V(λ) Test curve of corrected measurement head's cos spherical sensitivity

In the following paragraphs, I will prove the efficiency of my methods by measuring the time degradation of three solar panel types. In all cases, I placed the Minilux etalon by extending the tested solar panel's structural plane and by comparing the momentary power output to Energy Equipment Testing Service Ltd's PVMT 11250 Modul Tester device's measurement data.

To compare the measurement data conducted with the solar simulator accurately, I always registered the solar panels power output when the Minilux etalon showed 51.7 kilolux, and the solar panel had a temperature of 39 ^{0}C.

To start out with, I inspected two types of solar panels for which the artificial sun simulator was primarily prepared by the artificial solar simulator's manufacturer. One of them is a Korax KS 77 mono-crystalline silicon panel, and the other is a Kyocera made KC85GX polycrystalline solar panel.

In order to have a complete assessment, I have also completed the series of natural measurements on an amorphous silicon solar panel besides the mono-crystalline and polycrystalline solar panels, which I considered to be an unknown experimental solar panel in order to simulate an unknown GaAs type solar panel.

Fig. 3.15 shows the measurement results which prove that despite the characteristic differences, my method gives us certain values to the time degradation of the examined solar panels.

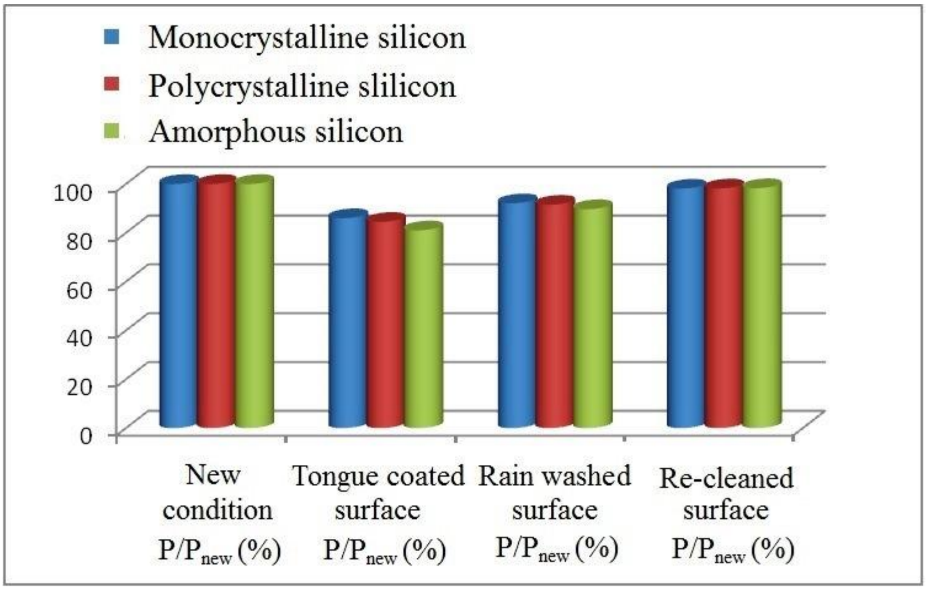

Fig. 3.15. Comparative measurements of mono-crystalline, poly-crystalline and amorphous silicon solar panels in natural conditions

The most useful conclusions of my method based on Fig. 3.15 is that the performance of solar panels is directly linked to degradation due to time and weather factors. It can also be concluded that the periodic usage of the method can decrease loss due to the weather by 10%.

3.5. Model for developing new types of semiconductor

Possessing the relevant information I collected by studying expansively the technical literature, I found that creating the GaAs-based solar cell structures is the most promising, since the absorption capacity of the GaAs-based solar cells is extremely good, its band gap reaches 1,4 eV and its efficiency can reach up to 30%.

The model (see Fig. 3.16) to create the new semiconductor needs to know the followings:

- semiconductor substrate: GaAs,
- manufacturing process: molecular epitaxy growth,
- manufacturing conditions: ultra-high vacuum space (10^{-11} mbar),
- low deposition temperature,
- growth in low speed (0.1-1 atomic row/s) under continuos control,
- using Knudsen-cells for composition and doping,
- in-situ monitoring the layer-growth with reflection high-energy 12 keV electron diffraction.

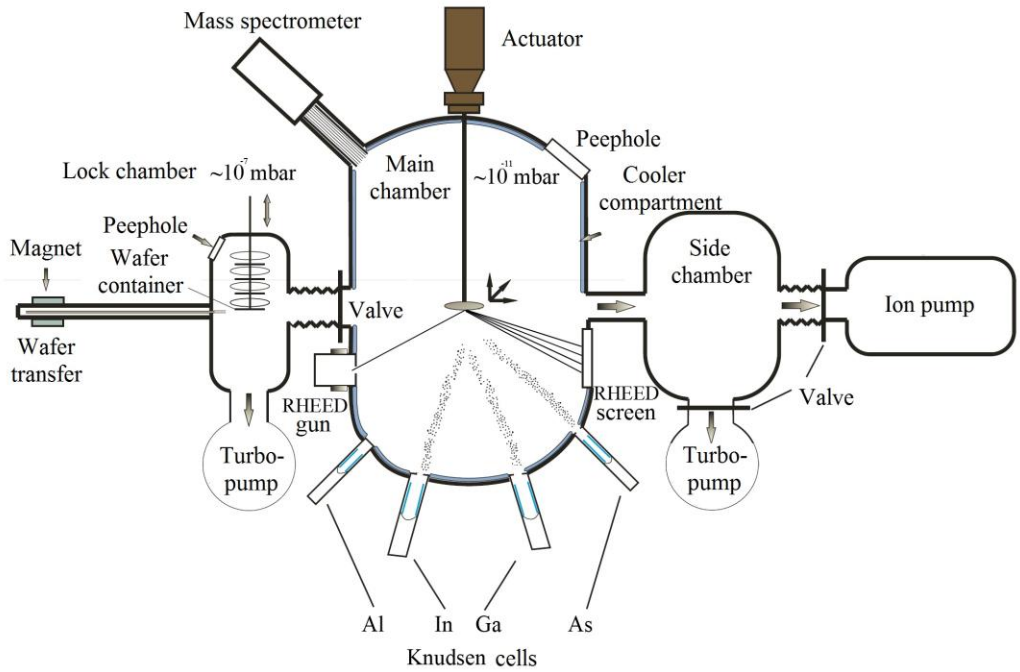

Fig. 3.16. The model figure of the MBE setup

The main chamber (reactor chamber) is in the centre of the model, where every layer-growth based procedure happens. In this space must be provided the best vacuum (10^{-11} mbar).

The most critical event of the layer-growth is the controlled emission of the molecular beam for wafer. For this procedure I chose into the system four (Ga, As, In, Al) - specifically for this purpose - effusion (also known as Knudsen) cells with traditional vertical orientation.

An important part of the main chamber is the reflection high-energy electron diffraction (RHEED), where a nearly 30 keV electron-beam is focused on the new solar cell's sample surface with less than a 4^{o} angle of incidence. With its help, the formation of the nanostructure on the wafer can be in-situ monitored. To all this belongs a phosphorus-coated fluorescent screen on the opposite side of the electron gun in order to visualize the nanostructure's RHEED mark.

To perform this precise detection, according to the RHEED electron ray's direction, the sample's plane must be adjustable. For this purpose, the planning of a special manipulator was needed, which can be moved in three directions, can be rotated and is operable outside the vacuum-chamber.

The development of the sample holder with the new principle was complicated, since the sample – regarding the large cleanness work space - has to be attached to an exchangeable sample support, which must be attachable from sample to sample on the special mover.

A molybdenum slippers form (see Fig. 3.17) was needed to be developed to hit the target, which - due to its three sided wedge development – eases the orientation to the final direction on the opposite shaped profile.

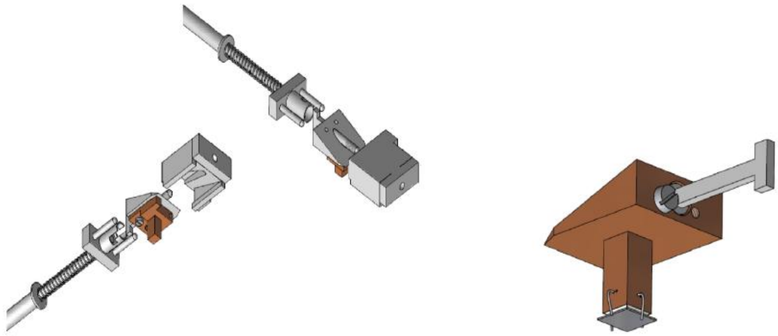

Fig. 3.17. The sample holder's movable and receiver unit

In the technological system of MBE as novelty, I used a connection similar to a sliding fork bayonet socket prestressed by a spiral-spring to the t-ended threaded arm shown in the Fig. 3.17. With this solution I ensure the sample holder's fall-proof mobility and secure it to its final position.

Thinking up the solvable coupling of the actual experimental wafer was a similar critical problem, which has to bare the random shaking during transport, as well as the thermal motion during vaporization, however the heat transfer must be provided between the wafer and its support. Besides its successful use in indium laboratories I worked out and used a spring holding as a novelty in MBE technologies shown in the Fig. 3.17.

3.6. Algorithm for controlling molecular current

One of the most relevant and critical issue of creating a new semiconductor based on molecule beam epitaxy is how to harmonize the in-situ measurement of the implanted molecules and - in parallel – controlling the molecular current. For this purpose I worked out a new, computer controllable shutter regulator algorithm, which regulates the current sources' (Knudsen cells) cryogenic pipe which produce the new semiconductor type. It works in such a way, that I observe the molecules' - coming on the experimantal samples - layer-construction period observable on the RHEED's fluorescent screen by a camera, which serves an image-processing unit. The image processor sends a command signal in a given phase of an appearing oscillation period's signal to the central unit, so that shutter regulator motors of the Knudsen cells block the path of the molecular current. With its help, a well-secured slip-less system can be accomplished for controlling the molecular current.

The control of layer-growth happens with a PLC-based cotrol system by computer monitor which can be seen on Fig. 3.18.

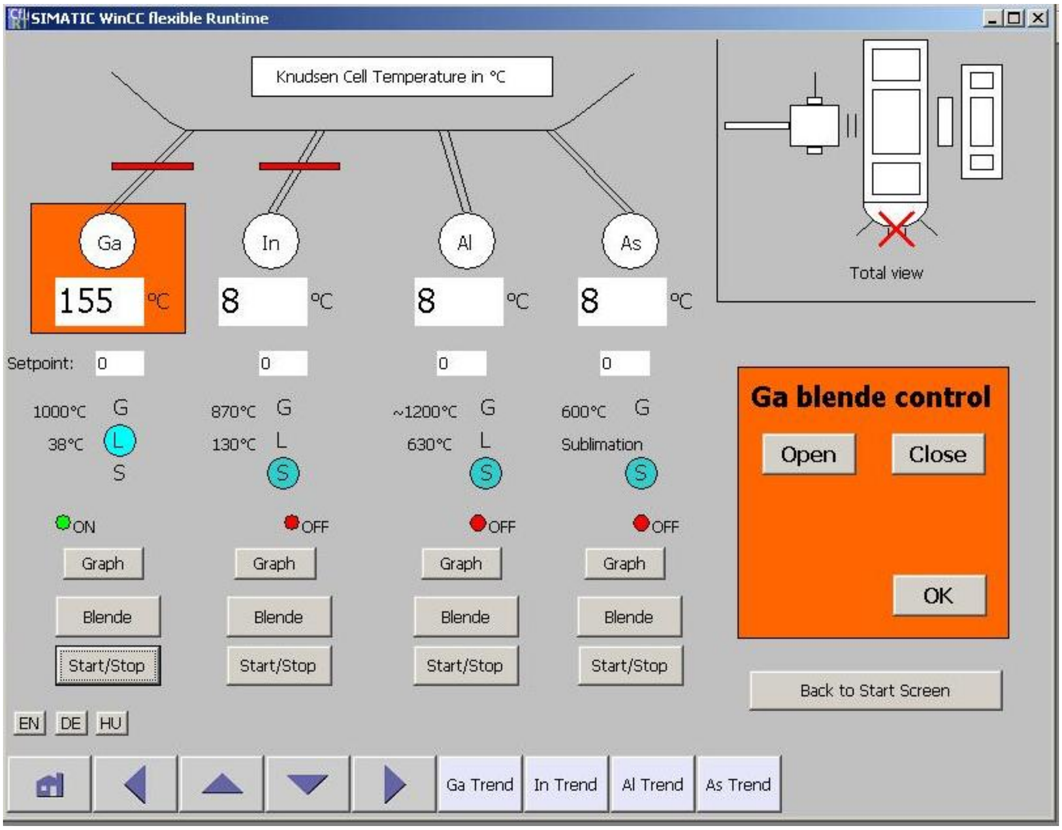

Fig. 3.18. Computer surface of Knudsen cell controlling

I accomplished the use of the PLC - which can be seen on Fig. 3.19 – with four communication lines: towards the process controller PC, which contains the monitor (see Fig. 3.18), towards the RHEED image-processing PC, towards the sub-unit, which measures and controls the Knudsen cells' temperature, and towards the sub-unit which monitores and controls the Knudsen cells' shutter mover motor.

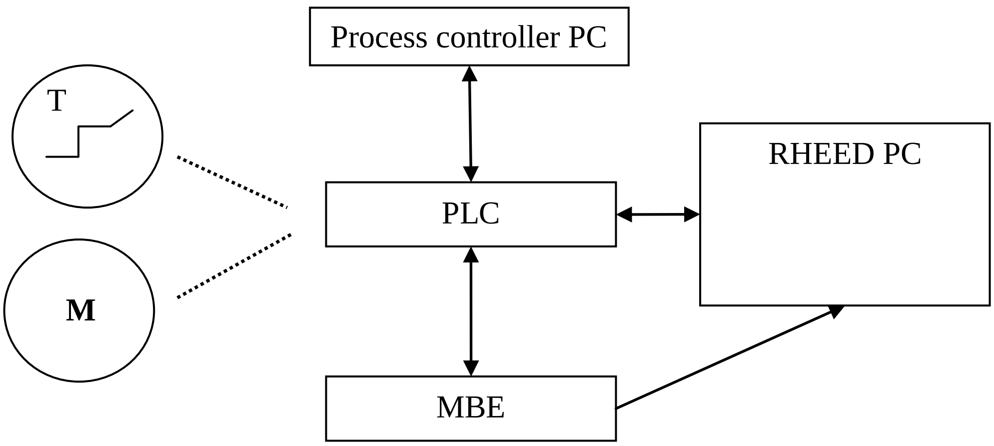

Fig. 3.19. Blocks of molecular current control system

According to the algorithm's security basic-step, the system at every turn-on must find and set back the Knudsen cells' unheated status and the closed state of the shutter as basic-status. From this state, motion only accures when something has been overwritten on the computer monitor with the help of the process controller PC's keyboard. For instance, when any of the Knudsen cells' temperature on the monitor gets modified to a higher value than room temperature, then - according to the algorithm - the PLC orders the RHEEDS's fluorescent screen's monitoring and data processing.
After the acknowledgement of the heated molecule source temperature, its shutter only opens to manual command. The closing can happen on one hand from the PC direction of the RHEED monitoring, if the detected signal is appropriate, on the other hand by the person carrying out the experiment, if it considers the current state of the process.

With this procedure, such regular crystal structure can be created on the substrate, where – in case of a properly selected GaAs mono crystal substrate – the grid structure of the grown layer can fit perfectly to the basic system of the substrate.

3.7. Evaluation of results

Three experiments have been conducted to test my thesis about the molecule beam epitaxic procedure with GaAs/InGaAs semiconducting structures. I used indium instead of aluminum for the active layer (InGaAs), because even the current vacuum value (10^{-8} mbar) does not cause oxidation problems and I can create a continuous layer with it. The first step was the vaporization of a clear, 0,5 μm thick GaAs layer on a 1x1 cm GaAs substrate, only then could the controlled InGaAs growth with the help of a RHEED image (see Fig. 3.19). I tested the process with three different thickness of active layers: 0,8 μm, 1 μm és 1,2 μm (see Fig. 3.20).

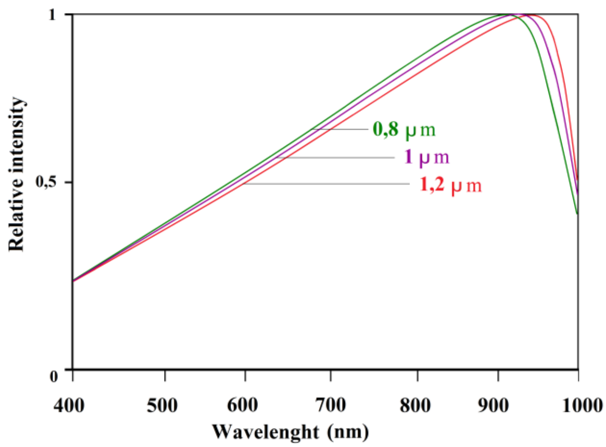

Fig. 3.20. Behaviour of detectors with InGaAs active layers of different thickness

The experiments verified that, by using the results of the broadband LED and detector made with LPE technology, my complex method can improve the energy conversion efficiency by 50% compared to what is known in literature.

4. NEW SCIENTIFIC RESULTS

New scientific results achieved during my research for the new type of solar cell and the optimal structure of the test are as follows:

1. I have developed a new, optical rating method that is free from superimpulse waves and provides traceable measurements of the various manufacturing stages of the solar panels carried out by monochromatic radiator that can be compared to internationally certified standards. As a detector calibrator, the method provides information on finished solar cells. And as a filter meter app, it provides an opportunity to improve the classification and technological process of the compound semiconductors and secondly to allow the optical optimization of all solar cell models whose front content layers are transparent.
2. I worked out a method to replace incandescent lamps with low-power semiconductor light source in infrared range. The essential element is a series of LEDs ranging between 1000-1700 nm, as a broad-spectrum energy converter. The method of production of certain components of the series is liquid phase epitaxy. I achieved to develop a concentrated light to the desired direction with minimal loss by creating different heterostructures, using semiconductors meeting each other at half-width wavelength beam. This method also served as the basis of the elaboration of the broad spectrum light elements.
3. Through my new spectrophotometric measuring method using the set-up steps of a series of LEDs ranging between 1000-1700 nm, I proved that a semiconductor layer structure detector (solar cell) can be created whose transformation of energy in a 1000-1650 nm range within ± 5% is wavelength independent.
4. I have developed a procedure that modifies spectral sensitivity, which can create a high precision detector from silicon light element that is aligned into the eye sensitivity curve to detect light from the solar panels. The procedure has made it possible to prepare a sensor device that can determine the current efficiency of any type of solar cell both outdoor and indoor application.
5. I set up a system type model required for the design of a new kind of semiconductor that is optimal in terms of solar cell. Based on the associated simulation and experimental results I developed a method which allows evaporating new type of solar cell samples in high security. The model has a new sample handling procedure which I developed. This procedure can be used in high vacuum combining the security of the industrial applications and the requirements of temperature precision of the laboratory application.
6. I have developed a new shutter-control algorithm, whereby an optional semiconductor type can be produced from the combination of the sample slice and different evaporatorators. With the algorithm, the molecule currents can be controlled to the extend that the number of molecules in the experimental samples is optimal in each phase.

5. CONCLUSIONS AND RECOMMENDATIONS

Today, one of the most promising trends in terms of the conversion efficiency of solar radiation energy is the creation of energy converters embracing a broad spectrum with semiconductor heterostructures.

The aim to be achieved for better efficiency is that the energy transformation must by all means happen within the p-n junction. Looking at the problem of the conversion of light energy via semiconductors from a reverse direction has proved to be very effective method for my aim to be achieved. Based on the experience and the results in the LED production, the convincing light energy conversion results have been achieved with the help of heterostructures made via liquid phase epitaxy (LPE) method which may play a significant role in the future due to its cost-effectiveness.

The first conclusion of the results is that the controlled growth of the semiconductor crystal layers and nanostructures is an important condition in creating more effective solar cell structures. These few atom-row-thin layers are prepared primarily by using molecular beam epitaxy (MBE) equipment.

The layers must be controlled (RHEED control) at the low-speed growth (0,1-1 atom row/sec) and thus the amount of the particles flying out of the Knudsen cell should also be regulated. I suggest monitoring the layers especially from the aspect of the self-organization, i.e. how the unordered pile of the elements is organized into arranged nanostructure through the interactions between the components. The accurate understanding of the organization mechanism and - based on this – the Knudsen-cell control are the key to develop the high efficiency semiconductor based solar cells with multiple quantum valleys and quantum points and high performance light emitting diodes in different wavelength radiation with different heterostructures.

Based on the method presented in my thesis I primarily suggest the production of the CIS solar cells, the single spectral organization of the sub-phases for the purpose of measurably better overall results.

Based on my results, I suggest a control measurement of each table of every PV panel - which I also used - in natural conditions on a monthly basis. With the help of evaluating the above results, the problems resulting in a reduced total energy production of the system can be filtered out in short time as well as feedback can be provided to the solar panel manufacturer in order to improve quality.

Finally I suggest – based on the above – the utilization of the new techniques and solutions not only in the production of a new type of solar cell, but also in the manufacturing of various special semiconductors that mainly light in infrared range.

6. SUMMARY

The biggest problem of our new millenium is the rising pollution due to maintain continued economic growth. This could slow down significally over the more efficient, accessable to all, decentralized renewable energy exploitation, where – for example – the sun is a continuous power transmitter. This is a means of increasing the efficiency of the widely utilizable semiconductor-based solar cells.

The main result is that I was able to demonstrate in laboratory with broadband energy converters of solid states, that the light emission and the luminous efficacy problems of the semiconductors are fundamentally the same. Utilizing the interoperability between two realisation processes, with test phases and part solutions received from the other, I was able to shape and improve the light emission and light utilization efficiency of hetero structures made by Liquid Phase Epitaxy(LPE) method. In summary, I created a highly efficient and widely used broadband energy transducer.

My other result is to develop an optical, system type model, which is necessary for evolving new types of semiconductors. This is made using a molecular beam epitaxial (MBE) equipment that can be controlled also in the preparation phase of the nanostructures. This is the most sophisticated and effective technique for the preparation of the zero-, one- and two-dimensional nanostructures.

At my system type model the formation of nanostructures can be kept under continuous (in situ) observation (RHEED control), which provides a way for particles to regulate the rate of transpiration.

My system integrated in situ control paved the way for the self-assembly mechanism for continuous monitoring of structures.

In this way we can always ensure the proper time and temperature for the emergence of the interaction between the particles, that is the formation of the ordered nanostructures by the preparation of the new solar cell.

My model is now able to plan ahead as the thickness of multiple quantum valleys, even the density of quantum dots, which is essencial for the production high-efficiency semiconductor solar cells, as well as different wavelength emitting, different hetero-structure, high-power light-emitting diodes.

I developed a new optical rating method, that helped to perform spectral optimizing certain/some phase products of the solar cell production as well as the evaluation of spectral sensitivity finished products, which is traceable to internationally certified standards.
Not only a new type of solar cell can be achieved in the future by the new methods and approaches, but also a variety of special lighting semiconductor devices.

7. MOST IMPORTANT PUBLICATIONS RELATED TO THE THESIS

Refereed papers in foreign languages:

1. Martin G., Muray K. **Réti I.**, Diós J., Schanda J. (1990): Miniature Integrating Sphere-Silicon Detector Combination for LED Total Power Measurement, Measurement 1990/8, pp. 84-89.
2. **Réti I.**, Giczi I., Muray K. (1993): Filter matching for imaging colorimetry, SPIE-The International Society for Optical Engineering, 1993/10, V32, pp. 2578-2580.
3. Rakovics V., Püspöki S., Balázs J., **Réti I.**, Frigeri C. (2002): Spectral characteristics of InP/InGaAsP Infrared Emitting Diodes grown by LPE, Materials Science and Engineering B – Solid State Materials for Advanced Technology 91-92: pp. 491-494.
4. Rakovics V., Balázs J., **Réti I.**, Püspöki S., Lábadi Z. (2003): Near-infrared transmission measurements on InGaAsP/InP LED wafers, Physica Status Solidi C 2003/3. pp. 956-960.
5. Szentpáli B., Berkó T., Molnár F., **Réti I.** (2006): Closed Space Electromagnetic Compatibility, Hungarian Academy of Scienses Research Institute for Technical Physics and Materials Science, Yearbook 2006. pp. 50-51.
6. Rakovics V., Püspöki S., **Réti I.** (2007): Output power saturation in InGaAsP/InP surface emitting LEDs, Hungarian Academy of Scienses Research Institute for Technical Physics and Materials Science, Yearbook 2007. pp. 42-43.
7. Rakovics V., Püspöki S., **Réti I.** (2009): Optimum design of InGaAsP/InP surface emitting LEDs for application in spectroscopy, Hungarian Academy of Scienses Research Institute for Technical Physics and Materials Science, Yearbook 2009. pp. 78-81.
8. Rakovics V., Püspöki S., **Réti I.** (2011): LPE growth and characterization of InP/InGaAsP infrared emitting diodes, Hungarian Academy of Scienses Research Institute for Technical Physics and Materials Science, Yearbook 2011. pp. 78-79.
9. **Réti I.** (2011): Technical background of very high efficiency GaAs based solar cell preparation, Research and Development, Mechanical Engineering Letters, pp. 216-226.
10. **Réti I.**, Ürmös A. (2012): MBE technology in the colourful LED and solar cell production, University of Óbuda e-Bulletin 2012/1, V3. pp. 191-203.
11. **Réti I.**, Farkas I. (2014): Some developments on molecular beam epitaxy technology for solar cell preparation, Hungarian Agricultural Engineering, No 25/2013, pp. 29-32.

Refereed papers in Hungarian:

12. Rácz M., Makai J., Ferenczi S., **Réti I.** (1989): Precíziós kézi fénysűrűségmérő, Automatizálás, 1989/7(1), 19-22. o.

13. Balázs J., Ferenczi S., Giczi I., Lánc J., Makai J., Rácz M., **Réti I.** (1991): Fotometriai és radiometriai mérések és műszerek, Villamosság, 1991/11(39), 343-346. o.

14. Rakovics V., Püspöki S., Serényi M., **Réti I.**, Balázs J., Bársony I. (2007): InGaAsP/ InP Infravörös diódák és lézerek, Hiradástechnika, 62:(10), 12-18. o.

15. Lukács I., Szabó J., Laczik Zs., Pődör B., **Réti I.**, Szentpáli B., Eördögh I. (2008): Makyoh topográfia, egy egyszerű és hatékony eljárás félvezető szeletek simaságának vizsgálatára, Hiradástechnika, 2008/63(1), 28-33. o.

16. Nemcsics Á., **Réti I.**, Tényi V. G., Kucsera P., Tóth L., Harmat P., Amadou M., Csutorás M., Kupás – Deák B., Sándor T., Bozsik J. (2010): Molekulasugár-epitaxiás nanostruktúrák előállításának műszaki feltételei, GÉP, LXI 2010/8, 29-32. o.

17. **Réti I.**, Farkas I. (2014): Optikai minősítő módszer a napelemek gyártási fázisaira, Magyar Energetika, 2014/1, 38-41. o.

18. **Réti I,** Ürmös A., Nádas J., Rakovics V. (2014): Nanostrukturás LED-ek, Elektrotechnika 2014/11, 19-21. o.