MBE Technology in the Colourful LED and Solar Cell Production

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Abstract: *It is well known, that the light emitting (radiative recombination and electroluminescence) and absorbing processes need special material properties and conditions. One of these fundamental conditions, is the direct band transition of the semiconductor material. This is a common property among the compound semiconductors. The production technology of devices significantly different from the ordinary silicon technology. In the creation of the device structure, the epitaxial growth plays an important role, during which similar crystal structures like the substrate, but some other different characteristics layers have grown. There are various methods and technologies of the layer growing by epitaxy. The Molecular Beam Epitaxy (MBE) stands out among the other procedures, because this is the most sophisticated and the most effective technique for the production of zero, one and two dimensional nanostructures. These semiconductor devices are revolutionized by these structures, including the light emission diodes and solar cells as well. In this article we will give a short introduction of MBE technique, and discuss about light emission diodes and solar cells, produced by this method.*

Keywords*: Molecular Beam Epitaxy; III-V materials; LED; Solar Cell; Quantum Well; Quantum Dot, color, pattern, harmony*

1 Introduction

In our work, we will present the production of the two large group of the optoelectronic devices (LEDs and Solar Cells) by the method of Molecular Beam Epitaxy.

The light emitting diodes - suchlike semiconductor PN junctions - emit light, if the suitable forward-bias was provided. Since their discovery, they have widely used and have gone through a large technological evolution in the past few years and decades. New kind of raw materials have appeared (InGaP/GaAs, GaInAlN/GaN) for their production. The best way to produce controlled fabrication of new semiconductor structures is the MBE.

Nowadays the most familiar and rapidly growing field of LED applications is the lighting technology. Its popularity has several reasons, for example it does not need maintenance, its costs are minimal, has a long lifetime and the energy consumption are low. Further advantages, that its light emitting direction is controllable, and we can create unique color experiences, thanks to its numerous color variant (for example desks for sale or the illumination of the storefront).

They are also widely used at home, in the offices as well, on the outer front of the buildings and in their inner rooms for general and emergency lighting, because of the low maintenance requirement of the LED lamps. They are common in public buildings, in the receiving rooms and lecture rooms as well. Because of their versatility they are used as a colourful reflector in stage technology [1], and for direct and backlighting of the artifacts (paintings, statues) in museums or in art galleries [2].

They have also a significant function in street lighting [3]. In the previous years numerous case studies have published, not only in abroad (California) [4], but in our country in Hódmezővásárhely [5] as well. In these applications there are some additional important viewpoints (towards the recently specified aspects) for example cost-effectiveness (the pay-off period can be planned) and the safety of operation.

During the last years the energy dependence has become larger and larger. The mankind recognized the risk, that the traditional fossil energy sources will be depleted. Due to this hazard, the interest turned to the direction of alternative energy sources.

Today the role of the solar cells become more and more important in the field of electricity supply, not only in extreme applications (for example in miscellaneous spacecrafts), but in everyday circumstances as well [6].

The solar cells are often used in ecological architecture [7,8,9], for the residential, public, agricultural and industrial buildings as well (Fig. 1.). In these applications an important question is the sunbathing. This means, that the light power strictly depends on the orientation and the other terrain features too. Generally it can be installed to the top of the buildings (on flat, tall and shallow roofs) or to the front side [7,8,10], but it can be used as a shadow seed as well.

Fig. 1. Thin film solar cells at the glass corridor of Technical College of München, from outside (left) and from inside (right).

The efficiency of the solar cells is between 5-15%. But the question remains in each case. How can we produce more electricity from the solar radiation? One of the possible method is, to grow different nanostructures (for example multi quantum-well, quantum dot) on GaAs substrate. According to the theoretical calculations the efficiency of multi quantum-well structures is above 40% and the quantum dot structure is over 60%.

In our work we will discuss about the LEDs and solar cells, made from the GaAs based nanostructures (quantum-well, quantum dot), made by Molecular Beam Epitaxy (MBE) [11,12].

2 Discussion

2.1 The Operation of LEDs

The operation of LEDs is based on the phenomena of so-called radiative recombination. The simplest way it appears in the forward-bias PN junction. This is the domain of the semiconductor crystal, where the conduction changes suddenly or with a transition from the change from p-type to n-type. If we set a forward-bias, then the height of the potential barrier decreases in front of the charge carriers. So the minority charge carriers can recombine with the majority charge carriers on the two sides of the junction (Fig. 2.). As we can see in this figure, the non-equilibrium charge carriers can recombine on local energy levels too. Due to this, they emit photons, so electromagnetic radiation appear. Therefore light is generated with a given color (wavelength), which depends on the width of the band gap [13,14,15,16].

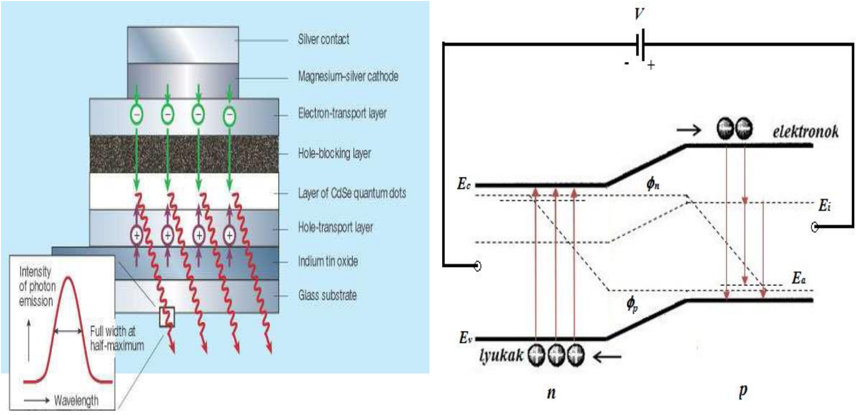

Fig. 2. In this picture there is a structure of the conventional LED (left side) and there is a forward-biased PN junction (right). The recombining charge carriers emit photons (red arrows).

For a long time, the researchers were not able to produce blue LED. The breakthrough was in 1993, when a japanese scientist Shuji Nakamura (Nichia Corporation) have studied GaN based nanostructures. One of his experiments was, when he was able to increase significantly the brightness of green, UV, blue and white LEDs. Nowadays, the white coloured versions are made from blue LEDs with different fluorescent powder (like in the light pipes), but the basic principles did not change.

2.2 Nanostructured LEDs

The III-N devices have many applications, because of their wide band gap. Particularly in the last decade become prevalent, not only in the short wavelength light sources, but at the high- speed and high-performance electronics as well.

In the active region of these devices there are one or more InGaN quantum well, sandwich-like wedged between the GaN layers. In the InGaN well the wavelength of the emitted light vary from ultraviolet to amber by changing of the InN-GaN ranges.

Although in present days we encounter high brightness nitride quantum well based LEDs in commerce, the studies have continued to increase the output light intensity of these devices. We can reach this goal more efficient, if we use quantum dots instead of quantum wells. The phase separated InGaN quantum dots cause the high brightness of the LEDs.

In Fig. 3. there is the heterostructure of the blue LED, in which two layers InGaN/GaN quantum dots have grown [17].

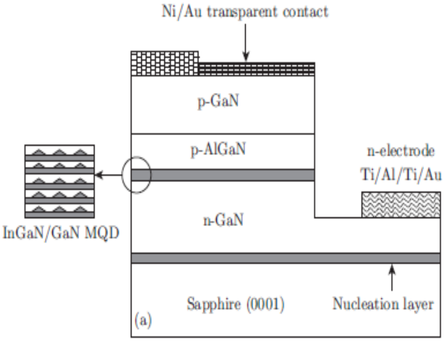

Fig. 3. Blue LED heterostructure (source: [17]).

2.3 The Operation of Solar Cells

The solar cell – similarly to LED – is a PN junction, which directly convert the energy of the sun to electicity [7,11,15]. The principle of its operation, that we generate free charge carriers by sunlight and separate them by a built–in electric field. The positive charge carriers accumulate on the “p” side and the negative charge carriers on the “n” side. In fact the energy comes from the majority charge carriers accumulated in the two layers.

The efficiency is an important property of the solar cell, which is a ratio of electrical power output and the incident light energy. To determine this feature, it is important factor the band structure of the semiconductor material (for example the width of the band gap). The reason of this, that the energy of the photons must be the same or larger than the width of the band gap. In the latter case, the additional energy will dissipate. If this energy is lower, then the photon cannot generate free charge carriers. The width of the semiconductor band gap is also dominant, because it is a problem, if it is too small (or too high) as well. According to the theoretical calculations, the optimum value of this property is 1.4eV (for example so matter is the GaAs) [7,11]. In the reality, the efficiency of different solar cell structures, differs from this, because of the losses (thermal, reflection, recombination) or cell constructions (in tandem or multi band solar cells). As we mentioned in the introduction, the efficiency of commercial silicon based cells is between 5-15%. The simple GaAs based PN structure solar cell also smaller than 30% too.

2.4 Nanostructured Solar Cells

To cross this limit by using of complex, so called multi band devices. The drawback of this method is the finite number of different semiconductors can be integrated and band gap width of these. The solution of this, is the using of different nanostructures (multi quantum well (MQW) and quantum dots (QD)) [11,12].

In the multi layer solar cells conatining quantum wells, the efficiency over 40 % is accessible by the using of the tuneling effect (Fig. 4.a.). Essentially the application of two different material with various band gap width, we create some quantum wells with dissimilar width. The possible energy state in the quantum wells can be set by the distance of the barriers.

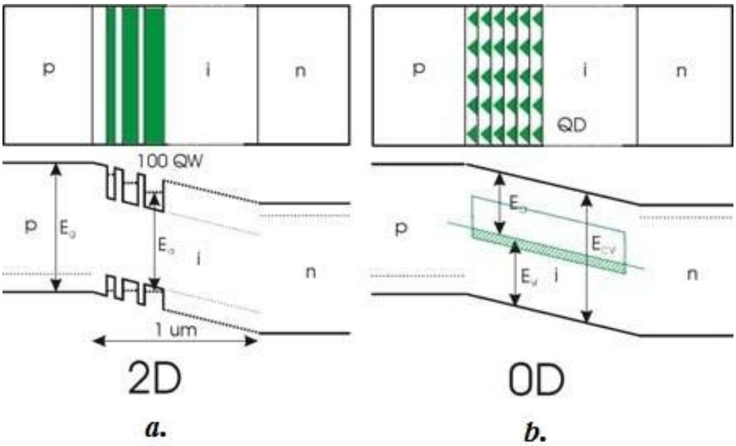

Fig. 4. The efficiency of the solar cell can be increased by using of quantum wells (a.) or quantum dots (b.) (source: [12]).

The excellent efficiency of these devices exceed the solar cells, containing quantum dots (Fig. 4.b.) [11,12]. In this technique we produce an inner band by quantum dots. This structure can absorb not only in energy levels of base semiconductors, but also in the middleware energy levels. In the case of the optimal sun energy conversion, the efficiency is above 60%.

This semiconductor structures can be made by molecular beam epitaxy (MBE).

3 The Technique of the Molecular Beam Epitaxy (MBE)

3.1 About this Technology

An important condition of the production of GaAs based solar cell and LED structure is the controlled growth of semiconductor crystal layers and nanostructures. These several atom row thick layers and other nano sized object mainly grow by molecular beam epitaxy (MBE, Fig. 5.) [18,19]. In this process is necessary a large mean free path and the ultra high vacuum (UHV) as well. The molecular sources (so called Knudsen cells) is directed to the sample holder and the particle flux can be controlled by temperature and by moving of the shutters above them. In case of III-V materials the deposition temperature is change between 200-550 ^{o}C.

Compared to the other procedure there are numerous advantages of MBE technique:

1. In one layer the low deposition temperature does not create fault location.
2. Reduce the possibility of interlayer diffusion.
3. Controlled low speed grow of the layers (0.1-1 atomic row/sec).
   a. The composition and doping of the material can change clearly by shutter opening or closing, above the Knudsen cells.
   b. Super lattices can be produced accurate with it.
   c. We can manufacture zero dimensional structures without expensive litography processes.

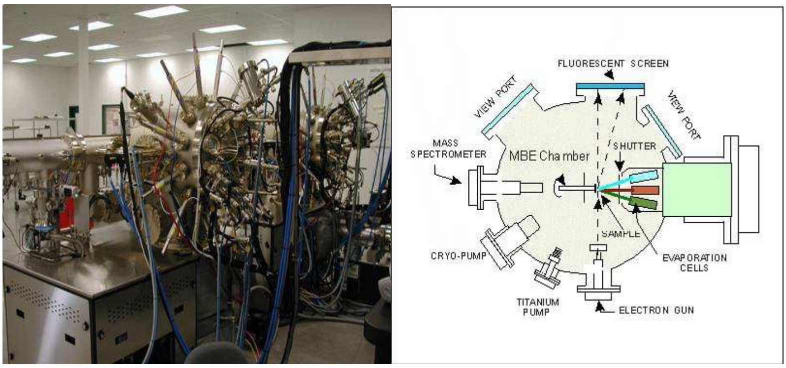

Fig. 5. A molecular beam epitaxy equipment from outside (left) and from inside (right).

In the next figure (Fig. 6.), we can folllow the progress of layer growing [20].

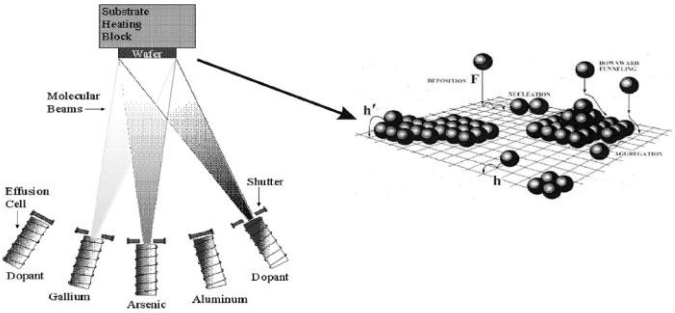

Fig. 6. The process of the layer growing (source: [20]).

Our MBE equiment [20] consists three parts (Fig. 7.). In the preparation chamber the pressure is 10^{-7} (10^{-8}) mbar. This chamber help us to put the sample into the main chamber without breaking the vacuum and without the risk of background contamination of the system. The next main part is the main chamber (the reactor chamber). This is the place of the layer deposition or another structure growing by atom or by molecular beam. These operations can be made in ultra high vacuum (10^{-10} mbar). So we provide, that the mean free path of particles will be large and the background contamination of the system will be low.

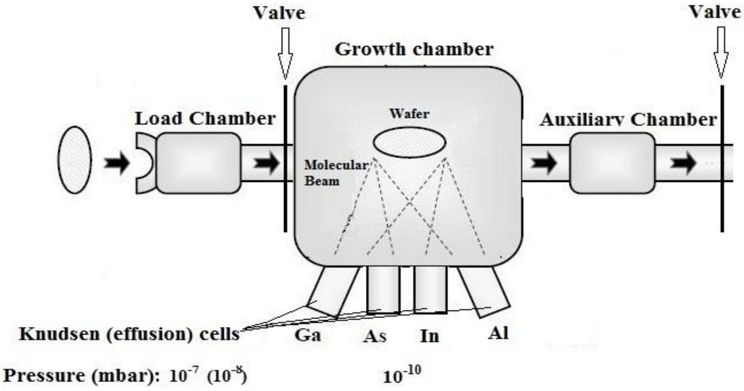

Fig. 7. The structure of the joint MBE equipment of TTK-MFA and the ÓE-MTI.

In the main chamber, the emission of the particle flux comes from the effusion (so called Knudsen cells), is directed to the sample. There are four cell in our system. We provide the molecular beam by the heating of this cells, which is necessary to the growth process. The sample is on a heatable precision manipulator. An important part of our instrument is the 12keV RHEED gun, so the growth progress can be examined by in-situ manner. With this method we can conclude, if an atomic layer is completed or which kind of nanostructures have grown on the sample (quantum dot, quantum well, quantum ring, double quantum ring or nano hole). Each of this structures have its own RHEED pattern, which is visible on a fluorescent screen, on the opposite side of the gun.

3.2 LED Technology

During the previous years, the researchers used many methods to made higher brightness LEDs. They have developed new encapsulation, heat dissipation and wafer-bonding procedures, as well as reflective surface substrates. So today well automated, but excellent efficiently light devices are made, in simple design for the first sight (Fig. 8.).

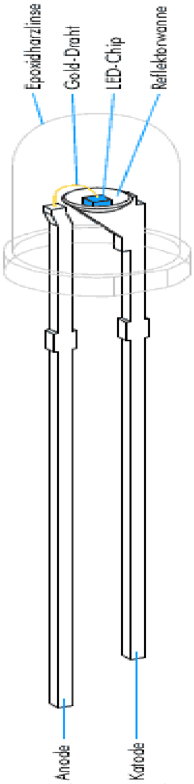

Fig. 8. LED on reflective surface substrate.

Another chance is to grow LED structures by Liquid Phase Epitaxy (LPE) [21,22] or by Molecular Beam Epitaxy (MBE) [23].

In this case there is also an advantage of the MBE method, that during the construction of heterostructures controlled thin films is formed, in order to the thin film (with other lattice constant) follows elastically the structure of the neighbouring thick film. So in the well of the mentioned InGaN structure, the wavelength of the emitted light is variable by the changing of the InN-GaN domains, from ultraviolet to amber.

These heterostructures can be made by the following way (source: [23]):

1. Grow GaN layer, on silicon substrate.
2. Clarify the substrate.
3. Absorbed gas evaporation.
4. Purify it in the place of growing.
5. AlN/GaN multi-layer deposition.
6. Grow n-GaN thin film.
7. Establish an InGaN/GaN quantum well.
8. Grow p-GaN layer.

3.3 Solar Cell Technology

A good example for the technology of nanostructured solar cells, is the experiment of the researchers at the University of Chulalongkorn (Bankok, Thailand) [24]. The scientists have grown self-assembled InAs quantum dots, on p-GaAs substrate. After the completion of buffer layer, they grow many layers (also in the self-assemled way) by low growth rate (0.01 ML/s), in 500 ^{o}C temperature. As a result large quantum dots with good quality were formed. After that an n-GaAs cover layer deposited, followed by an n-AlGaAs layer. Consequently three layers were on each other, containing quantum dots, in the PN heterojunction (Fig. 9.). The size and the density of quantum dots is controlled by the temperature and the growth rate of the capping layer and the substrate. By this method, the researchers reached, that their required quantized energy levels appeared in the nanostructure.

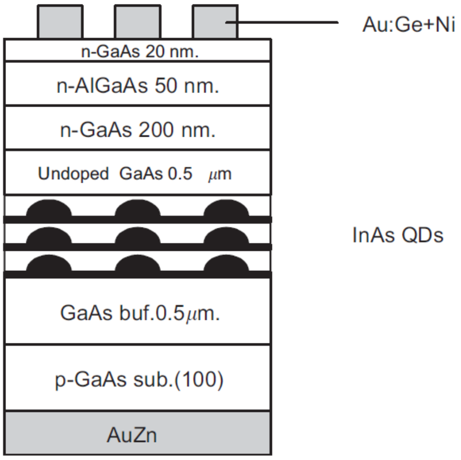

Fig. 9. The structure of a heterojunction, containing quantum dots (source: [24]).

An another possible approach is the idea of a Chinese research group, who have studied III-N type nanostructured solar cells (Fig. 10.) [17].

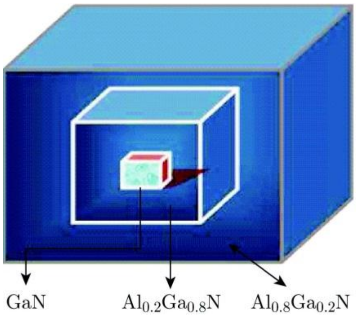

Fig. 10. Cube shaped GaN quantum dot, in an another larger $Al_{0.2}Ga_{0.8}N$ quantum dot (source: [17]).

4 Summary

As we have seen in the last two chapters the molecular beam epitaxy is a powerful, cheap and efficient procedure for the production of zero, one and two dimensional nanostructures. In our Institute the research and manufacture [21] [22] and metrology [25] of these light emitting diodes have several decades history. The actuality of our choice of topic is given by our molecular beam epitaxy system, installed in our institute [18,20], which allows us some new research and technology perspectives in this field as well.

References

[1] S. Böröcz, „LED színpadvilágítás 2011. - nagy meglepetések nélkül,” Óbudai Egyetem, http://www.vilagitas.org/stuff/3_led_konf/borocz_sandor.pdf, 2012.

[2] S. Ferenc, „LED-ek a múzeumvilágításban,” Óbudai Egyetem, http://www.vilagitas.org/stuff/3_led_konf/szabo_ferenc.pdf, 2012.

[3] S. János, „Szilárdtest fényforrások alkalmazása a közvilágításban, látásfizikai alapok,” in *Világítástechnikai évkönyv*, Világítástechnikai Társaság, 2010-2011, pp. 4-9.

[4] T. Cook, „LED Street Lighting,” City of San Francisco, California, http://apps1.eere.energy.gov/buildings/publications/pdfs/ssl/gateway_sf-streetlighting.pdf, 2008.

[5] I. Manz, T. Szőke, „A közvilágítás modernizációja LED-es lámpatestekkel Hódmezővásárhelyen,” Óbudai Egyetem, http://www.vilagitas.org/stuff/3_led_konf/szoke_tamas.pdf, 2012.

[6] P. Miklós, „Magyarország fotovillamos energetikai potenciálja,” *Energiagazdálkodás,* , 2004/6, 2004, pp. 7-10.

[7] Á. Nemcsics, A napelem működése, fajtái és alkalmazása, Budapest: BMF KVK 1188, 2005.

[8] Á. Nemcsics, „Napelemek az építészetben,” *Magyar Építőipar,* 2008, pp. 75-79.

[9] I. Farkas, „A napenergia hasznosításának hazai lehetőségei” *Magyar Tudomány,* 8. 2010, pp. 937-946.

[10] Á. Nemcsics, „Betekintés a napelemek világába (mőködés, fajták, alkalmazások),” Óbudai Egyetem, http://zoldegyetem.obuda.hu/wp-content/uploads/2010/08/nemesics_akos.pdf, 2010.

[11] Á. Nemcsics, „Új irányok a napelemes technológiában,” *Elektronikai Technológia, Mikrotechnika,* 2009, pp. 39-45.

[12] Á. Nemcsics, „Novel Alternative for the GaAs-based Self-organized Quantum-structure,” *Óbuda University e-Bulletin,* 2011, p. 1.

[13] Ö. Lendvay, Félvezető Lézerek, Budapest: Akadémiai Kiadó, 1985.

[14] E. S. Yang, Microelectronic Devices, New York: McGraw-Hill, 1988.

[15] S. M. Sze, Physics of Semiconductor Devices, New York: John Wiley & Sons, 1999.

[16] G. Held, Introduction to Light Emitting Diode Technology and Applications, New York: CRC PRESS, 2009.

[17] G. E. Weng, „III-Nitride-Based Quantum Dots and Their Optoelectronic Applications,” *Nano-Micro Letters,* 2011, pp. 200-207.

[18] Á. Nemcsics, I. Réti, V. G. Tényi, P. Kucsera, L. Tóth, P. Harmat, A. Mieville, M. Csutorás, B. Kupás-Deák, T. Sándor, J. Bozsik,

„Molekulasugár-epitaxiás nanostruktúrák előállításának műszaki feltételei,” *GÉP LXI.*, 2010, p. 29.

[19] M.A. Herman, H.Sitter, Molecular Beam Epitaxy (Fundamentals and Current Status), Berlin: Springer-Verlag, 1984.

[20] Á. Nemcsics, I. Réti, M. Serény, G. Tényi, R. Hodován, J. Gábor,I. G. Taar, J. Pántos, J. Bozsik, S. Molnár, R. M. Jankóné, „Beszámoló a BMF-MTI és az MTA-MFA közös laboratóriumában található MBE berendezés üzembe helyezéséről,” *Elektronikai Technológia, Mikrotechnika,* 2009, p. 33.

[21] V. Rakovics, J. Balázs, S. Püspöki, C. Frigeri, „Influence of LPE growth conditions ont he electroluminescence properties of InP/InGaAs(P) infrared emitting diodes,” *Mat. Sci. Eng. B80,* 2001, p. 18.

[22] V. Rakovics, S. Püspöki, J. Balázs, I. Réti, C. Frigeri, „Spectral characteristics of InGaAsP/InP infrared emitting diodes grown by LPE,” *Mat. Sci. Eng. B91-92,* 2002 , p. 491.

[23] M. Wakui, R. Ito, H. Sameshima, F.-R. Hu és K. Hane, „GaN-LED grown on Si substrate by MBE/MOCVD and monolithic fabrication of a light distribution variable device,” *Solid-State Sensors, Actuators and Microsystems Conference, 2009,* 21-25 June 2009, pp. 1349-1352.

[24] Suwaree Suraprapapich, „Quantum dot integration in heterostructure solar cells,” *Solar Energy Materials & Solar Cells,*2006, p. 2968–2974.

[25] G. Martin, K. Muray, I. Réti, J. Diós, J. Schanda, „Miniature integrating sphere – silicon detector combination for LED total power measurement,” *Measurement,* 1990, p. 84.