研 究 報 告 書

「高効率光電変換デバイスの実現に向けたIII族窒化物のマルチバンドエンジニアリング」

研究タイプ:通常型
研究期間: 平成 24 年 10 月～平成 27 年 03 月
研 究 者: サン リウエン

1. 研究のねらい

The aim of this research is to develop high-efficiency photo•electricity energy conversion devices based on III-Nitride semiconductors to ***realize full-spectrum absorption and light emitting***. The interface bandgap engineering for $In_xGa_{1-x}N$ films will be performed to realize *p*-type conductivity and fill the gaps in long-wavelength devices.

The photoelectric conversion efficiencies for the current existing optoelectronic devices are far from their ideality. For example, in the photovoltaic (PV) field, the current solar cells using Si, CuInGaSe, or GaAs-based materials are all concentrated on the long-wavelength absorption (< 2eV). To achieve the maximum conversion efficiency, full solar spectrum absorption using one material system is necessary. In the solid-state lighting (SSL) field, three-primary color (RGB) mixing is considered to be the most efficient method for generating white light compared to blue/ultraviolet LEDs with phosphors. However, RGB can not be realized by using one material system, which greatly increases the cost and lead to unnecessary efficiency loss during integration.

III-Nitride semiconductors (GaN, InN, AlN) exhibit the widest direct bandgaps among all the semiconductors, from near infrared (InN at 0.65 eV) to the deep UV range (AlN at 6.2 eV), which cover almost all the spectrum. This unique property makes the possibility of full-color light emitting and absorption devices using one material system, which will greatly improve the photo-electricity conversion efficiency and reduce the cost.

However, as a result of the high n-type background conductivity and strong surface electron accumulation, *p*-type doping in $In_xGa_{1-x}N$ remains a worldwide puzzle, which hinders the development of the long-wavelength absorption and emitting. The objective of this research is to ***solve the challenging problem in III-Nitride field of p-type doping in*** $In_xGa_{1-x}N$, and then ***develop full-spectrum photoelectricity energy conversion devices based on III-Nitrides, including high conversion efficiency PV cells and long-wavelength (620-700 nm) red LEDs***. To achieve this aim, we propose to ***deposit In-rich*** $In_xGa_{1-x}N$ ***at high pressures with the unique-designed MOCVD*** and ***the concept of multi-band polarization-induced hole doping for*** $In_xGa_{1-x}N$ ***through interface modulation***.

2. 研究成果

(1)概要

Superior to Si, Ge or GaAs-based semiconductors, direct-band gap material III-Nitride semiconductors, including GaN, InN, AlN and their ternary and quarternary alloys, is ***the only material system that can cover all the spectrum***. Moreover, they exhibit a number of unique physical and chemical properties, such as a large polarization field (MV/cm), high mobility, strong physical and chemical stabilization, ultra-high absorption coefficient (10^5/cm), and strong resistance against high-energy particle radiation. These features provide their promising applications in the SSL and ultra-high efficiency PV cells fields. In the SSL field, the invention of blue LEDs has been awarded to the Noble Price in Physics 2014, and up to now, high-brightness blue and green LEDs have been commercially used by $In_xGa_{1-x}N$ with a low In content (x<20%). However, one of the three primary colors red LEDs is usually achieved by AlGaInP materials, which make it difficult for a full technological integration. On the other hand, the current InGaN-based solar cells can only be achieved with an In content lower than 20% due to poor quality of $In_xGa_{1-x}N$ film, doping and devices. Therefore, although a high power conversion efficiency of 62% was expected for $In_xGa_{1-x}N$ multi-junction photovoltaic cells, the practical values are much small (< 4%). All the bottlenecks lie in the challenge of poor-quality In-rich $In_xGa_{1-x}N$ films and difficulty to realize *p*-type doping in $In_xGa_{1-x}N$ with a narrow bandgaps.

With the support from JST, during the three-year research in PRESTO, I have been concentrating on the development of InGaN films and *p*-type doping to achieve the full-spectrum absorption and emitting devices. To improve the quality of In-rich InGaN films, a high-pressure metal-organic chemical deposition (HPMOCVD) method was proposed to avoid the phase separation and alloy disorder. Due to the large equilibrium temperature of InN and GaN, once InGaN is deposited at high temperature, it is easily to be decomposed due to the low decomposition temperature of InN. On the other hand, if it is depsotited at low temperatures, the poor miscibility will lead to the phase separation and alloy disorder, which results in the bad surface and poor crystalline quality. Therefore, the only solution is to deposit InGaN films at high temperatures under high pressures, which can effectively suppress the InN decomposition. From considering the growth dynamics, a vertical-type flow-patterned MOCVD system which can be operated at as high as 4 atms was uniquely designed. The atomic level surface and interface control for InGaN films were achieved. On the other hand, to overcome the *p*-type doping difficulty from the high *n*-type background conductivity and surface electron accumulation, a novel physical strategy of multi-band polarization-induced doping method was proposed. The *p*-type hole concentration was achieved to be more than $10^{18}/cm^3$.

In addition, to fabricate photo•electricity energy conversion devices, the novel concept of intermediate-band (IB) transition was proposed to develop multi-level intermediate band solar cells. The IB solar cells showed a super-wide absorption from UV to near infrared region, covering almost all the strong luminescence of the solar light. Moreover, the full-spectrum light emitting LEDs especially the red light LEDs (>620 nm) were achieved by using InGaN-based quantum structures through interface control.

（2）詳細

Research theme 1: Design and develop the vertical-type high-pressure MOCVD for InGaN film growth (up to 4 atms)

To avoid the incorporation of impurities and reduce the *n*-type background, high temperature growth for InGaN is necessary. However, due to the weak bond of In-N, the InGaN will be decomposed easily with elevated temperature. According to the phase balance theory, the high pressure during growth is required to hinder the decomposition at high temperatures. Based on the growth dynamics of InGaN and the flow pattern optimization at high pressures, we have designed and established a vertical type MOCVD system which can operate at the pressures up to 4 atms. Figure. 1 shows the configuration of HPMOCVD. The standby vacuum level in the reactor chamber is as low as 10^{-6} torr to avoid the incorporation of impurities. A pumping system together with a pressure controller was used to automatically control and keep the pressure stably during growth. At high pressures, the inhomogeneity is usually considered to be a drawback for the film. Therefore, the gas introduction flow pattern was modified to a closed-coupled showerhead shape to improve the homogeneity at high pressures.

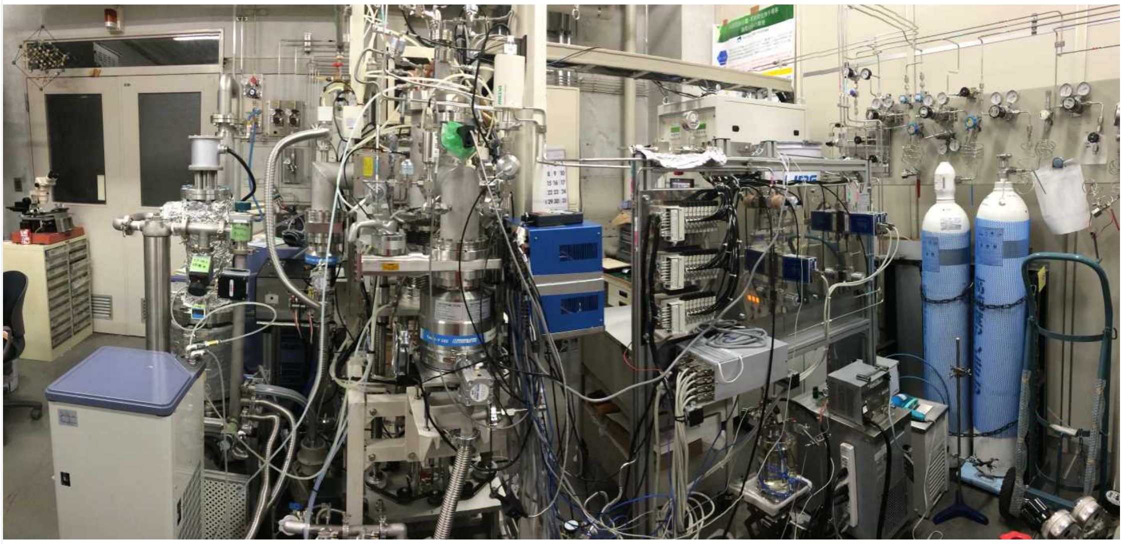


Figure. 1 Configuration of our developed HPMOCVD

Up to now, InGaN films with different In composition from 0 to 100% can be obtained by HPMOCVD system with the support of molecule beam epitaxy technique as illustrated in Fig. 2. The surface morphology of InGaN films grown by HPMOCVD can be controlled very well, as can be seen from Fig. 3. In the XRD 2θ-ω scan of InGan film, many interference peaks around InGaN peak indicates a very good interface between InGaN and GaN template. Figure. 3 (a) is the atomic force microscopy (AFM) image of the InGaN surface. The atomic steps can be clearly seen with a surface roughness lower than 1 nm. The InGaN/GaN short-period superlattices with interface in nanoscale were successfully obtained. Nitrogen is used as the carrier gas to improve the interface quality. Figure 3 (b) is the Z-contrast high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the superlattices structure. From this image, only the information from atomic number can be distinguished. As can be seen, very sharp interface without any interface layers or reactions is obtained.

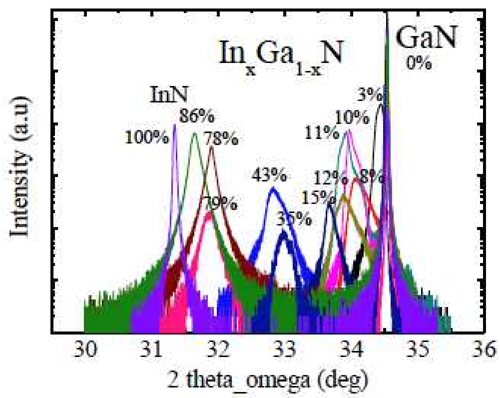
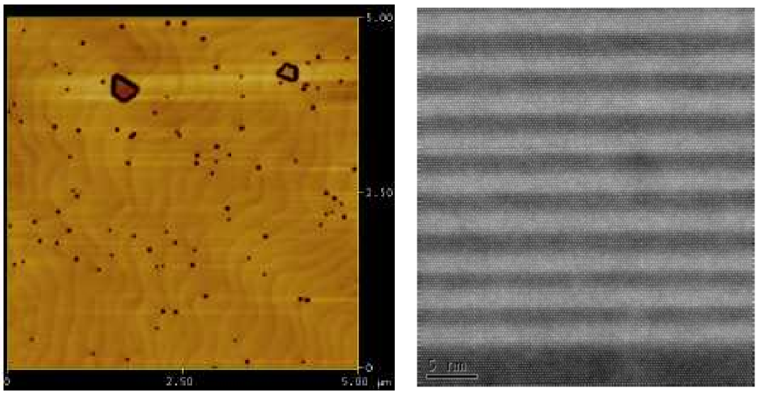


Figure.2 XRD 2θ-ω of InGaN film with In composition from 0 to 100%



(a) (b)

Figure 3 (a) AFM surface morphology of InGaN film grown by HPMOCVD; (b) Z-contract STEM image of InGaN/GaN superlattices

Research theme 2: Improving *p*-type InGaN by polarization-induced multi-layer structures through the interface band engineering

To obtain sharp interface for the heterojunction and multilayer structures, a smooth surface morphology for *p*-GaN is very important. However, the surface is always deteriorated due to the Mg dopants. By carefully modulating the dopant level, smooth surface for *p*-GaN has been achieved. The root mean roughness (rms) of 0.35 nm for *p*-GaN with the thickness of 1.5 μm was obtained. The growth of the heterojunction was also optimized. The thickness of *p*-InGaN is found to play the most important role for the hole mobility. A high mobility of 9.5 cm^2/Vs is obtained when the growth time of *p*-InGaN is 12 min. P-InGaN with In composition gradient multilayers were also designed and fabricated. The In composition was modulated by changing the growth temperature of *p*-InGaN multilayers. From XRD, In composition gradient InGaN layers are clearly observed. However, p-InGaN still shows a coherent growth on p-GaN, which guarantees a stronger piezoelectric polarization field. From CL measurement, the In composition along the growth direction in p-InGaN is changed from 7.9% to 35% (Fig. 4).

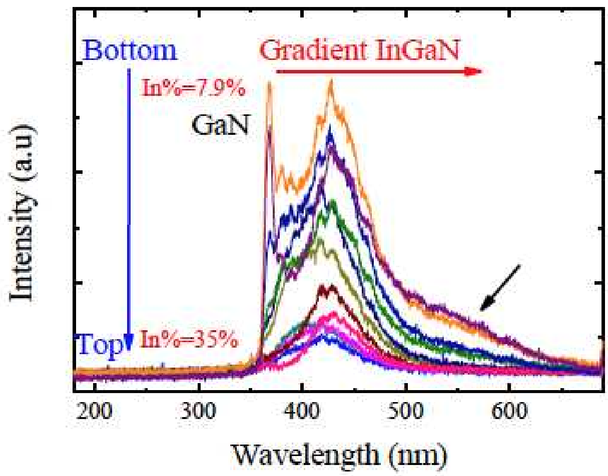


Fig. 4 Cross-sectional CL measurement of sample D, from which, In composition along the growth direction can be estimated.

Research theme 3: ***For the fist time***, propose and experimentally realize the concept of multi-level intermediate bands for Nitride solar cells and obtain a super-wide near full-spectrum absorption

The concept of intermediate-band transition was first proposed by Luque and Marti in 1997. It consists of an IB material sandwiched between two ordinary *n*- and *p*-type semiconductors, in which the sub-bandgap-energy photons are absorbed through the transitions from the valence band (VB) to the IB and from the IB to the conduction band (CB), adding up to the photovoltaic current. From this perspective, the short-circuit current density (J_{sc}) is greatly enhanced compared with that of the single energy gap *p-n* junction, while the open-circuit voltage (V_{oc}) can be maintained. Theoretically, the IB solar cells provide additional tolerance to match the solar spectrum toward a maximum conversion efficiency by modulating the energy level of the IBs. The predicted conversion efficiency for the single-IB solar cell is 63% under full concentration. However, all these devices require a high-quality wide-bandgap host material. From this perspective, III-Nitride InGaN is the best choice since its unique property is the high-quality GaN and low-In InGaN.

The intermediate sub-bands from InGaN quantum dots (QDs) are introduced in the InGaN *p-n* junction as the active region. To form multi-levels, three different kinds of quantum dots with different In composition and size are introduced. The formation of the mini-bands is further confimed from both experiment and theoretical estimation. This is the first time for achieving intermediate-band transitions in the III-Nitride field.

Figure 5 illustrates the experimental demonstration of intermediate sub-bands including cathodoluminescence (CL), external quantum efficiency (EQE), and two-photon excitation measurement (TPE). Different from the single emission for the RS cell, several emissions are present in the CL spectra. In addition of the luminescence from GaN (363 nm), an emission located at 408 nm from the $In_{0.1}Ga_{0.9}N/GaN$ pre-strained layers is observed, whose In composition (9.96%) is the same as the experimental design. The strongest peak at 465 nm (2.67

eV) is originated from InGaN/GaN host material, which is usually stronger and has a higher energy bandgap than those of QDs emissions. The luminescences located at the lower energies (517, 541, 630 nm) are attributed to the emissions from the triple QDs with different In compositions.

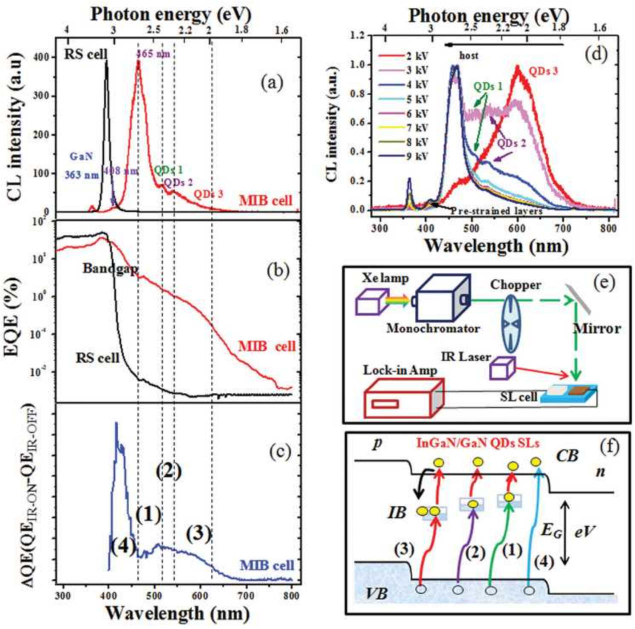


Figure. 5 Experimental demonstration of IB transition in Nitrides

Research theme 4: Demonstrate the proposed device concepts for solar cells and LEDs: conversion efficiency improved for solar cells and luminescence intensity increased for long-wavelength red light LEDs (~620 nm).

To demonstrate the proposed concept, p-InGaN with a In composition gradient layer was used for the p-type region of solar cells and LEDs. It was observed that J_{sc} of the InGaN-based solar cells was improved along with an increased conversion efficiency (Figure. 6). The improvement of the photocurrent is considered to be resulted from the improved hole concentration by using p-InGaN with In compositional gradient layer.

Although blue LEDs by using InGaN quantum wells have been well developed, achieving efficient operation of green light at longer wavelength (>500 nm) is challenging as In-rich InGaN quantum structures is difficult to fabricate with good interface. On the other hand, the large polarization field resulted from the great difference of In composition between active region and *p*-type region reduce the radiative recombination rates. To improve the luminescence efficiency of long-wavelength LEDs, the In compositional gradient InGaN layers were also utilized for the *p*-type region in the LED structure. The interface property was greatly improved compared to the p-InGaN/p-GaN structure. The LED showed a much stronger lumiscence at ~620 nm with a lower turned on voltage and leakage current (Fig. 7).

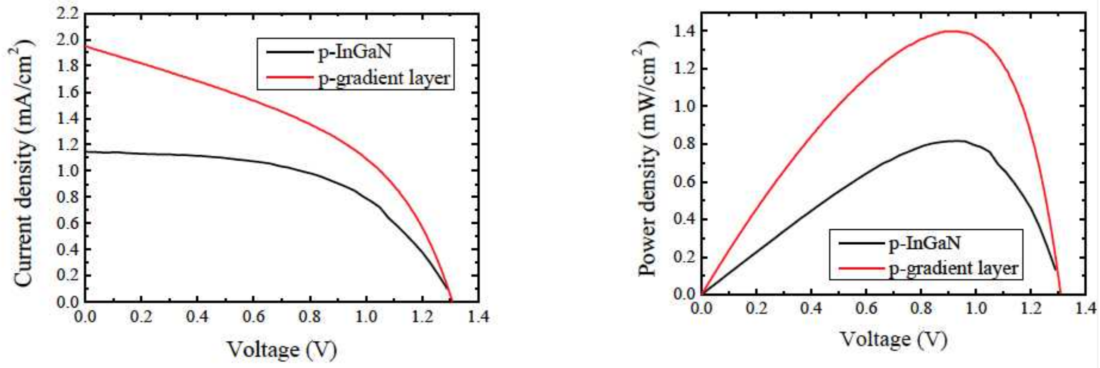


Figure. 6 Improved PV property of InGaN-solar cells by using p-InGaN In composition gradient layer

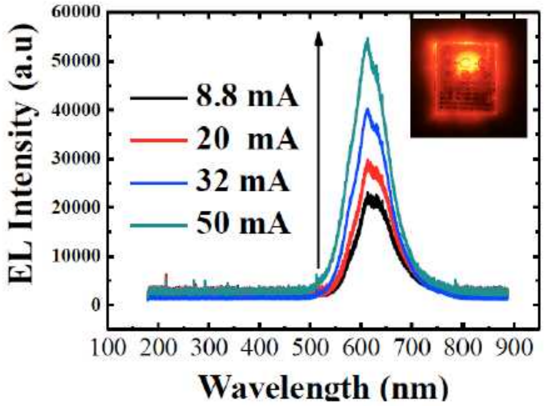


Figure. 7 Electroluminescence of red light LED

３． 今後の展開

Based on the research achievements, future research will be focused on:

<u>1) Further improve the HPMOCVD equipment for homogeneity of In-rich InGaN films:</u>

One of the biggest problems for the HP growth is the difficulty to obtain a good homogeneity. Although we have improved the uniformity of the InGaN films by modifying it into a showerhead shape flow pattern, at In-rich condition for InGaN films, the homogeneity still became deteriorated. More improvement such as changing the configuration design of the susceptor or carrier gas flow should be further considered.

<u>2) Extend the concept of multi-band engineering through interface control to more nitride-based devices</u>

We propose the concept of multi-band engineering through interface control, and realize multi-level intermediate band solar cells, improve the hole concentration of *p*-InGaN, and obtained the near full-spectrum nitride-based solar cells and LEDs. This concept is demonstrated to be effective for the nitride photo•electricity energy conversion devices. Further work will be concentrated to extend this concept to the electronic devices power integrated circuits.

4．　評価

（1）自己評価

（研究者）

During the three-year research life in PRESTO, I obtained many support from the advisors and members in this family. Compared to three years ago, my point of view not only for my research but also for the different fields was improved. This experience is and will be very important, valuable and helpful for my future research.

As for my own research progress, according to the initial research plan, the high-pressure MOCVD has been installed and high-quality of InGaN films have been achieved, p-InGaN with the proposed concept of polarization-induced multi-band modulation has been realized, and near full-spectrum absorption (multi-level IB solar cells covering the absorption from UV to near infrared region) and emitting devices (LEDs from UV to red light, especially realize red light emitting of 620 nm) have been obtained. The effect of my research is: 1) the proposed concept of interface control from the multi-band engineering for the Nitride photoelectronic devices will be helpful for nitrides to achieve the full-spectrum devices; 2) the success of p-channel FET by using InGaN heterojunction provide a new route for the nitride complementary logic circuit.

But there are still some drawbacks for my research. The conversion efficiency of the Nitride solar cells and luminescence efficiency of the long-wavelength LEDs still need to be improved. In the future, I will continue to work on high-pressure MOCVD to improve the InGaN film homogeneity, and further extend the concept of multi-band engineering to more devices.

（2）研究総括評価（本研究課題について、研究期間中に実施された、年2回の領域会議での評価フィードバックを踏まえつつ、以下の通り、事後評価を行った）。

（研究総括）

本さきがけ研究は、In（インジウム）含量の大きなInGaN（インジウム窒化ガリウム）薄膜を作成することで、赤外領域までを含む広い波長の太陽光を利用することで高効率な太陽電池の実現を目指す課題です。本研究を通じて、低効率ながら赤外領域までの太陽光の変換に成功し、また、内部構造に工夫（シャワーヘッド形ノズル化）した高圧MOCVD装置を実現し、40%を超える高いインジウム組成のInGaNの良質な薄膜作製に成功する等、当初提案を着実に進め、成果をあげたことを高く評価します。また、個人研究者として、言葉や文化の壁を越えて、当領域内の議論にも積極的に加わり、そこでの指摘を研究に生かした研究姿勢も評価いたします。

しかし残念ながら、太陽電池の高効率化という観点からは、開放電圧、変換効率とも低く、未だ課題が残っており、エネルギー高効率利用への寄与という観点では、不十分な成果となりました。今後は、本さきがけ研究で得られた多くの成果を生かし、太陽電池に限らず応用先を広く検討し、より大きな成果を実現して頂くことを期待します。

5．　主な研究成果リスト

（1）論文（原著論文）発表

1. Liwen Sang, Meiyong Liao, Qifeng Liang, Masaki Takeguchi, Benjamin Dierre, Bo Shen, Takashi Sekiguchi, Yasuo Koide, and Masatomo Sumiya, A Multilevel intermediate-band solar cell by InGaN/GaN quantum dots with a strain-modulated structure, Advanced Materials, 26, 1414-1420(2014), 2013 年 12 月発表 DOI: 10.1002/adma.201304335.
2. Liwen Sang, Meiyong Liao, Yasuo Koide, and Masatomo Sumiya, InGaN-based thin film solar cells: Epitaxy, structural design, and photovoltaic properties, Journal of Applied Physics, 117, 105706 (2015), 2015 年 3 月発表 DOI: 10.1063/1.4914908.
3. Liwen Sang, Junqing Hu, Rujia Zou, Yasuo Koide, and Meiyong Liao, Arbitrary Multicolor Photodetection by Hetero-integrated Semiconductor Nanostructures, Scientific Report, 3, 2368 (2013), 2013 年 8 月発表, DOI: 10.1038/srep02368.
4. Liwen Sang, Meiyong Liao, Yasuo Koide, and Masatomo Sumiya, Temperature and Light Intensity Dependence of Photocurrent Transport Mechanisms in InGaN p-i-n Homojunction Solar Cells, Jpn. J. Appl. Phys., 52, 08JF04 (2013) 2013 年 5 月発表
5. Liwen Sang, Meiyong Liao, and Masatomo Sumiya, A Comprehensive Review of Semiconductor Ultraviolet Photodetectors: From Thin Film to One-dimensional Nanostructures, Sensors, 13, 10482-10518, (2013) ***invited review*** 2013 年 8 月発表

（２）特許出願

研究期間累積件数:1 件

1.

発　明　者: サン　リウエン／リャオ　メイヨン／小出　康夫／胡　俊青／邹　儒佳
発明の名称: 半導体光検出器
出　願　人: 独立行政法人物質・材料研究機構
出　願　日: 平成２６年　２月　６日
出 願 番 号: 特願 2014-020952

（３）その他の成果（主要な学会発表、受賞、著作物、プレスリリース等）

主要な学会発表

招待講演

1. Liwen Sang, and Masatomo Sumiya, Photo・electricity energy conversion devices based on III-V nitride semiconductors, 2016 International Symposium toward the Future of Advanced Researchers in Shizuoka University, Invited, 2016 (Shizuoka University, Hamamatsu, 3rd March, 2016)

2. Liwen Sang, Meiyong Liao, and Masatomo Sumiya, Photoelectrical energy conversion devices based on III-Nitride semiconductors, IUPAC 9th International Conference on Novel Materials and Synthesis (NMS-IX) & 23rd International Symposium on Fine Chemistry and Functional Polymers (FCFP-XXIII), Invited, 2013 (Fudan University, Shanghai, 17th-24th, Oct, 2013)

口頭発表

1. Liwen Sang, Temperature dependence of photovoltaic properties in InGaN solar cells, 2015

MRS Spring Meeting&Exhibit, Oral (April 6th-10th, 2015, San Francisco, California, USA)

2. Liwen Sang, Meiyong Liao, Qifeng Liang, Masaki Takeguchi, Benjamin Dierre, Takashi Sekiguchi,Yasuo Koide, and Masatomo Sumiya, Multilevel intermediate-band solar cells based on III-Nitrides, 2013 年秋季第 74 回応用物理学会学術講演会, 同志社大学京田辺キャンパス, 2013 年 9 月 16 日(月) 〜 20 日(金)

3. Liwen Sang, Meiyong Liao, Qifeng Liang, Masaki Takeguchi, Benjamin Dierre, Takashi Sekiguchi,Yasuo Koide, and Masatomo Sumiya, Multilevel intermediate-band solar cells based on III-Nitrides, received by 10th International Conference on Nitride Semiconductors as the Oral Presentation, 2013 (Washiongton D.C. USA, 25th-30th, Aug, 2013)

4. Liwen Sang, III-Nitride semiconductors for high-efficiency energy conversion devices, MANA International Symposium 2013, Feb. 27-Mar. 1, 2013, Oral presentation.

5. Liwen Sang, Meiyong Liao, Yasuo Koide, and Masatomo Sumiya, Temperature dependence of photovoltaic properties in InGaN solar cells, 2013 年春季第 73 回応用物理学会学術講演会, 神奈川工科大学 , 2013 年 3 月 27 日（水）〜30 日（土）

6. Liwen Sang, Meiyong Liao, Yasuo Koide, and Masatomo Sumiya, Photoelectrical energy-conversion devices based on III-Nitride semiconductors, International Workshop on Nitride Semiconductors 2012, October 14-19, Sapporo, Japan, Oral.

受賞

1. 平成 24 年 10 月 25 日　ポスドク研究成果ポスター賞　InGaN 系光·電変換デバイス　独立行政法人物質·材料研究機構（受賞者氏名：桑立雯）

プレスリリース

1. 平成　25 年 12 月 06 日掲載、独立行政法人 科学技術振興機構、「InGaN の多重中間準位を活用した太陽電池の高効率化の原理を実証」

2. 平成　25 年 12 月 06 日掲載、日経 web 刊、「JST など、InGaN の多重中間準位を活用した太陽電池の高効率化の原理を実証」

6.. その他関連の情報

（1）新たに構築した研究ネットワーク：相手先名称、概要が非公開の場合には「非公開」と記載

相手先分類	相手先名称	形態	概要
Osaka University	Prof. Yusuke Mori	GaN bulk	Discussion on the substrate treatment and regrowth technique
Peking University (China)	Prof. Xinqiang Wang Prof. Bo Shen	InN template, InGaN films by MBE	Discussion on the growth of InGaN films by HPMOCVD and MBE, provide InN template
NIMS	Dr. Yasutaka Imanaka Dr. Kanji Takehana	Transport property	Help to measure and analyze the transport property of the samples

（2）研究会・領域会議での助言・指導による研究課題の進め方、方向修正等について

During this three-year research life in PRESTO of Phase interface field, I leant a lot not only from the point view of research but also the attitude to the research. All the advisors are so supportive and serious for me. They teach me how to express my research to the audience, how to show my research to the researchers who are not in the same field, how to think out of my own research but from the whole point of view, how to find the collaboration from different field, etc. Especially, I remember when I first made presentation in the PRESTO meeting, nobody could understand what I was talking about since we are from different fields and I was too nervous to explain clearly. Prof. Hashimoto gave me very strict comment. He said a good researcher should explain his research clearly and make the people who are not in his field understand. Otherwise, he could not get improvement but just a mediocre researcher. The PRESTO researchers should not be like that. Actually, I was very sad at that time. But I totally understand and agree with him. I know my weak point. I always tied to show all of my results to the audience but forgot the audience are not in the same field with me, and they could not understand me at all if I could not explain to them by using easy words. After that meeting, I have been learning to explain my research achievement in a more understandable way. I started not to show everything but just to explain like telling a story. This kind of training is very helpful to me. The scientific research should not be difficult to understand. We should make the public to understand what we are doing and how our research can contribute the daily life. Then we can contribute to the society.

I also got many good friends. We can discuss the problems in research, and also talk about some problems in the daily life. I expect future collaboration with them.

This experience in PRESTO is a great treasure for my whole life. I am so appreciative that I could have the chance to join this project and this family three years ago.

（3）さきがけ期間を通じて研究手法、実用化への考え方、取組み方で学んだこと

The important thing I learnt from PRESTO is to try to find the common point and collaborate with researchers in different field. The scientific research should not be hidden or bound in a small place. Researchers need to talk, to communicate, and to discuss. Through collaboration among different field, we can find the innovations and improvement.