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研究課題名（和文）Investigation of co-doped GaAs:NSb/AlGaAs IBSC with ideal transition energies for high efficiency Solar Cells

研究課題名（英文）Investigation of co-doped GaAs:NSb/AlGaAs IBSC with ideal transition energies for high efficiency Solar Cells

研究代表者

エルボーグ　マーティン（Elborg, Martin）

国立研究開発法人物質・材料研究機構・若手国際研究センター・ＩＣＹＳ研究員

研究者番号：６０７２４６３０

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研究成果の概要（和文）：高効率の可能性が期待されている中間バンド型太陽電池（IBSC）を対象に、窒素ドープGaAs量子井戸について材料およびデバイスの観点から研究を進めた。光学計測から窒素組成と局在準位との相関を明らかにするとともに、キャパシタンス分光によってこの窒素由来のエネルギー準位の評価を行った。結晶成長では窒素組成を制御し理論モデルに近いエネルギー配置のGaNAs/AlGaAs量子井戸の作製を行うとともに、窒素とアンチモンの同時ドーピング法による光学特性の改善を実現した。窒素量を増やすと実効バンドギャップは縮小するが素子の開放電圧は増大する興味深い知見を得た。この結果はIBSCの研究を進める大きな成果である。

研究成果の概要（英文）：We study dilute-N GaAs quantum wells (QWs) for application in Intermediate Band Solar Cells (IBSCs) with proposed conversion efficiencies exceeding the Schokley-Queisser limit of single-junction solar cells. We investigate the optical properties of GaNAs QWs exhibiting both confined quantum states as well as optically active N-induced defect states. The energy levels are characterized by capacitance spectroscopic techniques (DLTS, Admittance, CV measurement). We optimize the epitaxial growth to achieve close-to-ideal transition energies in GaNAs/AlGaAs QWs. Co-doping with Sb leads to improved optical quality. Using a strain-free GaAs/AlGaAs quantum dot model system, we demonstrate clear two-step photocurrent generation at room temperature, the key IBSC operating principle. We realize a recovery of open-circuit voltage in GaNAs/AlGaAs QW embedded solar cells for deeply confined structures. Our results represent a major advancement in the pursuit to realize the IBSC concept.

研究分野：物質科学

キーワード：太陽電池　量子構造　MBE，エピタキシャル　GaNAs　中間バンド太陽電池　2段階光子吸収　開路電圧

１．研究開始当初の背景

To increase solar cell efficiencies is a most pressing issue to make photovoltaic electricity generation more economical and to allow a clean energy generation of the future. To overcome the efficiency limitations of standard solar cells, several new concepts have been proposed, so called Third Generation Photovoltaics. The Intermediate Band Solar Cell (IBSC) is one of the most promising Third Generation Phtovoltaics concepts with the prospect of largely exceeding the theoretical maximum efficiency of regular single-junction solar cells. Under full concentration of sun light the theoretically predicted conversion efficiency exceeds 60% [1]. In an IBSC, as illustrated in Fig. 1, an additional photocurrent is generated from sub-band gap energy photons by a two-step photon absorption process via intermediate energy states while maintaining the high open-circuit voltage of the larger band gap material.

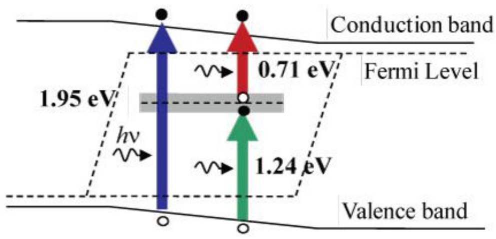

Fig. 1: Schematic of the **I**ntermediate **B**and **S**olar **C**ell concept.

The topic has recently attracted considerable research attention. Still at an early stage, the concept has not yet been proven experimentally and some fundamental challenges need to be overcome. Until now, research on quantum structured IBSCs has largely been limited to the lattice-mismatched In(Ga)As/GaAs material system, in which QDs are grown by Stranski-Krastanov growth mode since it is a well-established technique. However, the shallow confinement energies in this material system (~100 meV) make it impossible to achieve appropriate transition energies (IB at 700 meV) to realize highly efficient IBSCs and do not suppress thermal carrier escape from the IB energy states, a process that is not compatible with the IBSC concept. Research on new material systems is required to overcome these limitations.

To further the understanding of the operating principle of IBSC as well as to work on overcoming the fundamental challenges of realizing a working IBSC, we are investigating quantum structures of dilute-N GaAs/AlGaAs quantum wells (QWs) towards achieving an experimental demonstration of the operating principles of IBSCs. To increase the optical quality of dilute-N GaAs, which can degrade due to N-induced defects, we investigate the improvement by co-doping with Sb. For comparison we study strain-free GaAs/AlGaAs quantum dots (QDs) as a model system with very high crystal quality.

２．研究の目的

Understanding of physics of IBSC:

- Open-circuit voltage (V_{OC}) relation to confinement depth of quantum structure
- Dependence of two-step photocurrent on carrier accumulation in dependence on carrier escape and recombination rates
- Achieve material combination for IBSC research with close-to-ideal transition energies using GaNAs/AlGaAs

Crystal growth and solar cell fabrication:

- Realize deep confinement in GaNAs quantum structures by tuning N concentration
- Possible improvement in crystal quality by Sb co-doping
- Characterize energy states of confined and defect states to improve material quality
- Analyze relation of confined quantum states and N-induced defect states

３．研究の方法

Crystal growth: Samples are grown by molecular beam epitaxy (MBE). Our machine is equipped with a Nitrogen radio-frequency plasma source as well as Ga, Al, Sb evaporation cells, Si and Be evaporation cells for n- and p-doping, and a valved As source. P-i-n diode structures are grown as AlGaAs host material and form the basic solar cell structure. Embedded in the i-region we grow GaNAs QWs or GaAs QDs which provide confined energy states below the band gap which act as intermediate energy states.

Solar cell device fabrication: The grown samples are fabricated into solar cell devices by pattering the sample by photolithography for contact formation and mesa-etch. These devices with a defined contact area and window for illumination are suitable both for solar cell characterization as well as capacitance spectroscopic techniques.

Material characterization: To characterize material composition and surface properties, high resolution x-ray diffraction and atomic force microscopy is employed. Photo- luminescence experiments are carried out to gain an understanding of the optically active confined and defect energy levels in the materials.

Device characterization: The device properties are analyzed using

current-voltage and photocurrent spectrum measurements. The obtained results are used to optimize the structure in regard to solar cell performance, preventing tunneling and thermal escape as well as reducing recombination rate of IB carriers.
Two-light illumination: To demonstrate the two-step photocurrent generation of an IBSC a special two light illumination setup is necessary for characterization.
DLTS measurement: The deep level transient spectroscopy (DLTS) is a very powerful measurement technique which has not yet been applied for the study of IBSCs. Using this electrical space-charge technique, we characterize the present energy levels (both quantum confined energy states as well as possible defect energy levels) in the IBSC structure.

４．研究成果

During the funding period we were able to make significant progress towards the goal of understanding the physical mechanisms of quantum structure embedded solar cells and towards achieving a practical Intermediate Band Solar Cell. The dilute-N GaAs material system proved to have a high potential for realizing a experimental realization of an IBSC. The main results are organized in five sections.

(1) Characterization of the GaNAs/AlGaAs material system

We fabricated GaN_xAs_{1-x} (x = 0 – 3%) quantum wells (QWs) embedded in AlGaAs and investigated their optical transitions by means of absorption and emission experiments. As observed from PL experiments, with increasing N concentration a strong red-shift of the QW transition energy is achieved, which yields deeply confined intermediate energy states precisely tunable by their N concentration which is important for achieving the proposed IBSC transition energies. Photocurrent spectra, which are closely linked to the density of states demonstrates that these states are effective in generating an additional photocurrent from sub-band gap photon absorption. Embedding GaNAs in wider band gap AlGaAs makes it possible to observe their absorption characteristics over a wide spectral range which revealed distinct increases in photocurrent generation originating from transitions at higher energies above the QW ground state. Analyzing the photoluminescence emission we observe the co-existence of N-induced energy states and QW confined states. [2]

(2) Improvement in optical quality of GaNAs quantum structures by Sb co-doping

Dilute-N GaAs is an interesting material for optoelectronic applications due to its wide tuneability of band gap energy originating from an extremely large bowing coefficient for the incorporation of N into GaAs. However, when N is incorporated in GaAs, crystal quality commonly degrades, due to the very small atomic radius and high electronegativity of the N atom. To compensate for the induced strain around N incorporation sites, we investigate the co-incorporation of larger Sb atoms during the molecular beam epitaxy growth. We determined the Sb incorporation rates under different Sb flux, substrate temperature, and growth modes, i.e. continues growth and growth interruptions.

The Sb incorporation into GaAs is found 1) to be strongly dependent on substrate temperature where at lower temperature incorporation is higher, 2) to increase with Sb flux set by the Sb cell temperature, and 3) during a growth interruption step (only As supplied during growth interruption) Sb desorbs proportional to the growth interruption time from the surface. With the determined growth rates we grew GaNAs QW samples with and without Sb co-incorporation. Judging from photoluminescence emission intensity as shown in Fig. 2 the crystal quality improved. This improvement is stronger in the as grown samples and is only marginal in the samples annealed by rapid thermal annealing at 800°C after the growth. The shift in emission wavelength is associated with the change in band gap energy due to Sb incorporation which needs to be designed in combination with N concentration to achieve the desired structures. The technique of Sb incorporation to improve the crystal quality of GaNAs is effective; however the approach needs to be balanced with the higher complexity of the material system when introducing an additional element.

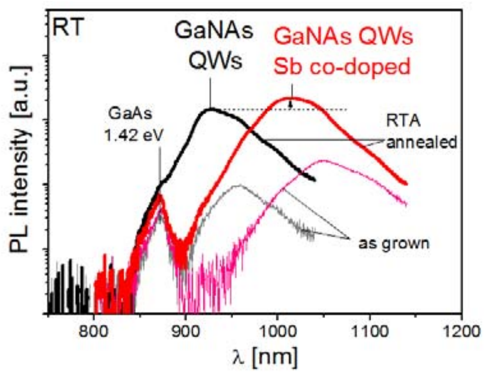

Fig. 2: Photoluminescence spectra of GaNAs QW samples with and without Sb co-incorporation for as grown and post-growth annealed samples.

(3) Understanding of the two-step photocurrent generation process

To gain a better understanding of the physical processes in IBSC, we investigate GaAs/AlGaAs quantum dot embedded solar cells which are completely strain-free and therefore have an advantage in material quality and simplicity over the GaNAs/AlGaAs material system at present. Although the GaAs/AlGaAs quantum dot energies are only very shallow and therefore not suitable for a practical Intermediate Band Solar Cell, the fundamental physics of the two-step photon absorption process via these intermediate energy states can be investigated well in this model system.

Using molecular beam epitaxy growth, we fabricate a quantum structure of GaAs/AlGaAs droplet epitaxy quantum dots (QDs) with artificial wetting layer (see Fig. 3 a)) embedded in a p-i-n solar cell structure. We are able to observe a clear two-step photocurrent generation at room temperature. This process in which carriers are excited in a two-step photon absorption process from valance band via IB energy states to the conduction band is the key operating mechanism of IBSCs.

A first light (780 nm) photo-excites carries in the QD confined energy states and not in the AlGaAs solar cell since photon energy is below AlGaAs band gap energy. The current-voltage characteristics under this illumination condition at room temperature are shown in Fig. 3 b). When a second light of 1500 nm is illuminated additional to the first light, we observe a clear increase in absolute photocurrent generation (see Fig. 3 c)). We find that the two-step photocurrent generation depends largely on the applied bias and exhibits a maximum at -0.3 V. A notable feature is a monotonic decrease in two-step photocurrent in the forward bias region, where the operating point of the solar cell lies. Using a model of rate equations, we extract the voltage dependence of the individual escape and recombination rates, and found that the decrease in two-step photocurrent in the forward bias region is related to a monotonic decrease in electron population in the quantum dots. Such analysis of the voltage-dependence of two-step photocurrent generation is indispensable to understand the physical processes in such a solar cell under operating condition. [3]

(4) Achieving high open-circuit voltage in solar cells with embedded deep confined quantum structures

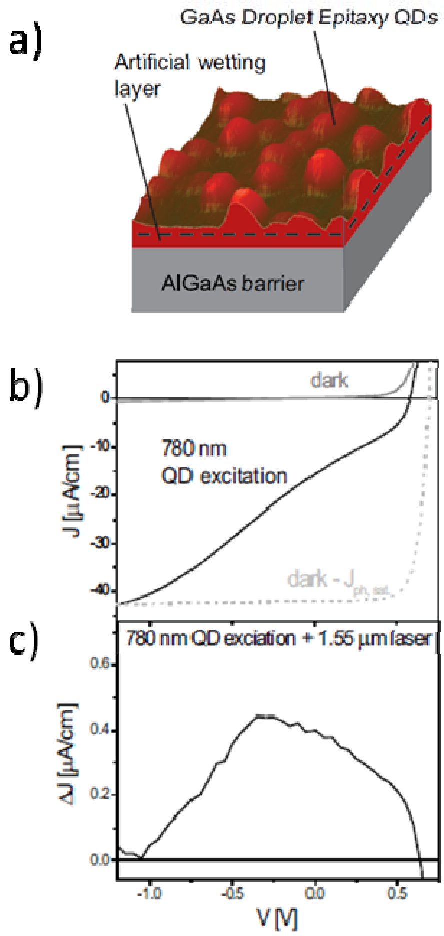

Fig. 3: (a) 3D atomic force microscopy image of the QDs with underlying artificial wetting layer, (b) Current density-voltage characteristics under QD excitation and (c) voltage dependence of the two-step photocurrent signal. [3]

Progress in IBSC research has been achieved in the successful observation and study of the two-step photocurrent generation process. For practical photovoltaic power output of the solar cell it is equally important to investigate the voltage at which this current is generated. Taking open-circuit voltage as a measure to judge the ability of the solar cell to achieve the maximum power point at a high voltage, research shows that open-circuit voltage of solar cells with embedded quantum structures is commonly degraded compared to a reference without quantum structure. One possible reason for this degradation is the process of carriers escaping from IB states by thermal-assisted tunneling which is possible due to the shallow confinement depth of the quantum structures. To understand and prevent such voltage degradation we systematically study quantum structure with varying confinement depth.

Using dilute-N GaAs quantum wells (QWs) embedded in an AlGaAs host solar cell, we study the dependence of open-circuit voltage on confinement depth of the embedded QWs which can be precisely tuned by adjusting the N concentration. A sample series of GaNAs QWs with N concentrations ranging from 0…3% has been grown by molecular beam epitaxy. Open-circuit voltage initially degrades with the incorporation of shallow GaAs QWs (N = 0%) into AlGaAs compared to an AlGaAs reference solar cell without QWs. For these shallow confinements, open-circuit voltage is limited by the lowest band-band transition, i.e. QW transition. With higher N concentrations of the GaNAs QWs (N ≥ 0.5%), open-circuit voltage does not degrade further and starts to recovers towards the highest N concentration of 3.1%. Current-voltage characteristics revealed that complete suppression of thermal/tunneling carrier escape from the QWs is achieved for N concentrations ≥ 0.5%. Therefore, by preventing any thermal/tunneling escape of carriers from the QW, the open-circuit voltage is no longer limited by the QW transition. Deeply confined GaNAs QWs with higher N concentrations exhibit a small offset band-gap to open-circuit voltage offset, as small as 0.23 V in the highest N sample, which is beyond the limit achievable in bulk semiconductor solar cells. Such higher open-circuit voltage in relation to the lowest band-to-band transition energy in a material holds great promise for the realization of IBSCs. [4]

(5) Characterization of energy levels by Deep Level Transient Spectroscopy (DLTS)

DLTS is the ideal characterization method to gain the necessary information about the confined energy levels concerning their activation energies, escape time constants, and capture cross-sections. While DLTS is commonly applied for the investigation of defect states, we are applying this technique to quantum structure embedded solar cells to analyze the present quantum confined energy states as well as possible defect energy levels.

A clear DLTS signal is measureable in the p-i-n diode structure with GaAs/AlGaAs QDs embedded in the middle of the i-region. In collaboration with Prof. Bollmann of Technical University Freiberg in Germany, we were able to measure the structure under standard DLTS setup with a bias pulse applied (Fig. 4 a)) as well as modify the setup to enable photon excited DLTS measurements by exciting the sample by a pulsed LED emitting at the wavelength of the QD absorption (Fig. 4 b).

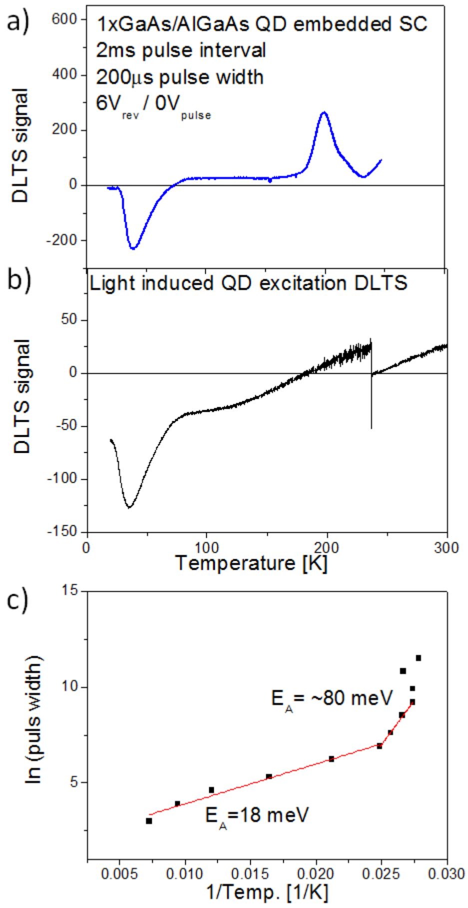

Fig. 4: a) DLTS signal in standard setup and b) QD excitation light induced DLTS measurement of 1×GaAs/AlGaAs QD embedded solar cell. c) Arrhenius plot of the DLTS peak at 40K.

In such experiments we now are able to observe selectively the signal originating from carriers escaping the quantum structure. This is important to distinguish DLTS signals originating from other parts of the solar cell structure such as defect states in the bulk material. We characterize the signal from the QD structure by determining its activation energy from an Arrhenius plot (Fig. 4 c)). We find that these minority carriers (negative DLTS signal) in the QDs exhibit an activation energy of ~80 meV at low temperature and 18 meV at temperatures > 50 K. The possible origin is the carrier escape from the confined QD level at low temperature, while at higher temperature their escape from the shallower two-dimensional wetting layer is dominant.

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５．主な発表論文等
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〔図書〕（計　－　件）

〔産業財産権〕
○出願状況（計　－　件）
○取得状況（計　－　件）

〔その他〕
ホームページ等

６．研究組織
(1)研究代表者
エルボーグ　マーティン
(Elborg, Martin)
国立研究開発法人物質・材料研究機構・若手国際研究センター・ＩＣＹＳ研究員
研究者番号：60724630

(2)研究分担者
（　　　）
研究者番号：

(3)連携研究者
（　　　）
研究者番号：

(4)研究協力者
野田　武司　(Noda Takeshi)

間野　高明　(Mano Takaaki)

佐久間　芳樹　(Sakuma Yoshiki)

Joachim Bollmann

Andre Venter

Danielle Venter