Position-Controlled III–V Compound Semiconductor Nanowire Solar Cells by Selective-Area Metal–Organic Vapor Phase Epitaxy

Takashi Fukui, Masatoshi Yoshimura,
Eiji Nakai, Katsuhiko Tomioka

Abstract We demonstrate position-controlled III–V semiconductor nanowires (NWs) by using selective-area metal–organic vapor phase epitaxy and their application to solar cells. Efficiency of 4.23% is achieved for InP core–shell NW solar cells. We form a ‘flexible NW array’ without a substrate, which has the advantage of saving natural resources over conventional thin film photovoltaic devices. Four junction NW solar cells with over 50% efficiency are proposed and discussed.

Keywords Solar cell · InP · Semiconductor nanowire · Photovoltaic

INTRODUCTION

Semiconductor nanowires (NWs) have attracted much attention for use in future nanometer-scale electronic and optical devices (Hiruma et al. 1995; Gudiksen et al. 2002), because they have small diameters and large surface areas that enable the fabrication of various kinds of functional devices through the use of p–n junction or hetero-junction structures. For example, the NWs of axial hetero-junction structures with highly lattice-mismatched materials can be formed, and growth in the radial direction succeeding axial growth enables the formation of core–shell (CS) or core–multishell (CMS) NWs. The use of axial or CS NWs provides considerable functionality to NW-based devices.

The main approach to grow NWs is based on a vapor–liquid–solid (VLS) mechanism (Wagner and Ellis 1964), which uses catalysts and liquid phase underneath metal particles for crystallization. VLS-grown III–V compound semiconductor nano-whiskers were investigated in the early 1990s (Hiruma et al. 1991). The potential of NWs to be applied to future electronics and photonics was demonstrated

in the early 2000s after this pioneering work (Gudiksen et al. 2002; Björk et al. 2002). Since then, the VLS method has become exceedingly common because it can be used to synthesize almost all semiconductor NWs through rather simple procedures. However, it sometimes encounters difficulties in forming axial hetero-junctions with sharp interfaces and forming CMS NWs by changing the growth direction. Accordingly, the self-catalyzed method has recently been investigated as a means of growing NWs to avoid the unintended generation of impurities (Morrall et al. 2008).

Another approach to grow NWs is catalyst-free selective-area growth. Selective-area metal–organic vapor phase epitaxy (SA-MOVPE) is a kind of template method, which involves a combination of bottom-up (epitaxial growth) and top-down (lithography) approaches. This enables the fabrication of nanostructures with lithographically defined positioning. The masks used with this method are usually amorphous film, such as SiO₂ and SiN_x. The use of (111) B-oriented substrates enables the formation of both inclined {110} facets and vertical {1-10} facets. The formation of only {1-10} vertical facets on a (111)B-oriented surface has been demonstrated by Fukui et al. (1990). After that, vertical hexagonal nanostructures could be formed by using selectivity to form {1-10} facets, and these structures were thereafter applied to laser and photonic crystals.

This approach can be applied to grow NWs by using smaller mask openings. Position-controlled polygonal nanostructures surrounded by several facets can be formed inside the openings, because crystal continues to grow through the mechanism of faceting growth. Because the direction of preferential growth for III–V NWs is the $\langle 111 \rangle$ A or $\langle 111 \rangle$ B directions, the use of III–V (111)A or B substrates enables the formation of vertically aligned hexagonal pillars surrounded by {1-10} vertical sidewalls. These position-controlled NWs

have been achieved in III–V compound semiconductors, such as GaAs (Noborisaka et al. 2005) and InP (Mohan et al. 2005). Position-controlled CS NWs, CMS NWs, and axial heterostructure NWs have also been reported. This paper reports on our recent work on the position-controlled growth of III–V NWs by applying SA-MOVPE to solar cell applications.

PHOTOVOLTAIC APPLICATION OF III–V SEMICONDUCTOR NWS

In photovoltaic applications, the periodic NW array structure has the potential to improve optical absorption while reducing optical reflections. It is predicted that CS structures with radial p–n junction (Hu and Chen 2007), which are aligned parallel to incident light, will improve the collection efficiency of photo-generated electrons and holes across the junction area. Moreover, this structure has the advantage of saving natural resources over conventional thin film photovoltaic devices. These advantages can be demonstrated by utilizing a well aligned array of high quality NWs. A lot of photovoltaic applications of NWs have been reported (Tian et al. 2007; Kelzenberg et al. 2008; Colombo et al. 2009; Czaban et al. 2009; Borgström et al. 2011), but comparatively few periodically aligned NWs with uniform CS structures have been fabricated thus far. We have recently fabricated highly uniform InP CS NWs with radial p–n junctions and demonstrated InP NW-based photovoltaic devices. Figure 1 shows a schematic view of an InP CS NW solar cell on a p-InP substrate.

InP has an appropriate bandgap energy of 1.34 eV for solar cell application at room temperature. The CS III–V NWs grown by SA-MOVPE provide both geometrical and electrical advantages for photovoltaic applications.

The growth conditions for core p-type InP NWs were described in Goto et al. (2009). The sequences of crystal growth for intrinsic and n-type InP shell layers were carried out continuously by changing the growth conditions. The T_G was decreased to 570°C to grow the shell layer and the partial pressure of TBP was increased to 1.6×10^{-4} atm to enhance lateral growth. The molar flow ratio of SiH_4/TMI was 5.67×10^{-3} during the growth of n-type shell layers. Although the dopant concentration was not investigated in any layer of CS NWs, secondary ion mass spectrometry (SIMS) analysis of the thin film crystal grown outside the NW array revealed that the concentration of Zn in the p-type layer was 6×10^{18} atoms cm^{-3} and that of Si in the n-type layers was 1×10^{18} atoms cm^{-3} . A Zn concentration of up to 2×10^{18} atoms cm^{-3} was also detected in the intrinsic layer between p–n junction. This was probably due either to the memory effect of the Zn dopant inside the growth chamber or Zn diffusion from the p-type core region.

Figure 2 shows a scanning electron microscope (SEM) image of an InP CS NW array. The average diameter of core InP NWs was 135 nm and this was almost equal to that of the holes in the SiO_2 mask pattern. This means that core NWs mainly grew perpendicular to the substrate, i.e., in the $\langle 111 \rangle_A$ direction, with little lateral growth. After the shell layer had been grown, the diameter increased and

Fig. 1 Schematic view of InP CS NW solar cell on p-InP substrate

Fig. 2 Scanning electron microscope (SEM) image of InP CS NW array

became 180 nm on average. This increased diameter suggests the formation of a radial p–n junction as a CS structure. The NW array grown by SA-MOVPE was rather dense compared with the VLS NW array, and the filling factor was 20%. Such a dense NW array was produced as a result of controlling the position and direction of all NWs grown by SA-MOVPE.

We fabricated a photovoltaic device using a CS p–n junction InP NW array covering an area of 1.0 mm × 1.0 mm on a p-type InP (111)A substrate. Figure 3 shows a cross-section SEM image of an InP CS NW solar cell. We used an indium tin oxide (ITO) film as a transparent electrode for the photovoltaic devices. ITO film was sputtered on the NW array at RT, followed by heat treatment at 400°C to reduce the resistance of ITO. ITO deposited quaquaversally on the some long wires due to the large steps. Then, an Ag electrode as a carrier collector was formed on the transparent

Fig. 3 Cross-section SEM image of InP CS NW solar cell

ITO electrode. An Au–Zn alloy ohmic contact was also formed on the back of the InP substrate. The chip was a triangle with sides of 6 mm and the active NW area consisted of 0.683 mm × 0.683 mm segments. The active area contained NW interspaces but excluded domains that were covered with Au electrode connecting the whole array. The photovoltaic performance was measured under air-mass 1.5 global (AM1.5G) illumination, where the radiation intensity was calibrated using a reference cell module just before measurement was carried out.

Figure 4 plots the I – V characteristics of the InP NW array cell. The device had an open circuit voltage (V_{OC}) of 0.674 V, a short circuit current (J_{SC}) of 11.1 mA cm^{−2}, and a fill factor (FF) of 0.585, which corresponds to an overall efficiency of 4.23%. The current density and efficiency were determined on the basis of the active area. This efficiency was much smaller than that of normal InP planar devices (Sugo et al. 1985) because the growth conditions and layer thicknesses for our devices were not optimized.

Many issues still remain for improving NW solar cell efficiency. For instance, more accurate and controlled doping are required to reduce both contact and series resistances. The size of the NWs should also be optimized to achieve better matching with the diffusion length of electrons in a p-type region as predicted from theoretical calculations (Hu and Chen 2007). Non-uniform arrays and NW thickness fluctuation may also reduce the efficiency of present devices. Additional surface passivation should suppress the radial built-in electric field and decrease the surface recombination with photo-generated electrons and holes. For example, in this work the InP wire surfaces will be covered with a wider band gap material (AlInP) and the resultant decrease in the surface recombination of generated carriers will increase solar cell efficiency.

FUTURE PROSPECTS FOR NW SOLAR CELLS

We also demonstrate a ‘flexible NW array’ without a substrate. The interface stress between the wires and substrate makes it easy to remove the wire part after all the device processes have been completed. Furthermore, this enables the substrate to be reproducibly used. We confirmed uniform NW array growth on re-used patterned substrates. If a substrate could be used many times, it would greatly reduce the cost of NW solar cells. This flexible NW solar cell array is advantageous in that, compared with conventional solar cells, it requires two orders less of semiconductor materials for electric power generation. For example, a NW solar cell with 15% efficiency requires only 6 mg of semiconductor material (InP) to generate 1 W of electric power, while 3.3 g of silicon is needed for a commercially available silicon solar cell with the same efficiency.

Fig. 4 Plots of InP NW array cell I – V characteristics

Another important feature of semiconductor NWs is hetero-junction formation with highly lattice-mismatched materials. Good quality axial hetero-junction NWs can be formed despite high lattice mismatched. For example, no threading dislocation is formed in 200-nm diameter NWs with as much as 3% lattice mismatched (Glas 2006). This is an important advantage for multi-junction NW solar cell formation. Up to now, the highest solar cell efficiency in three-junction cells under the global AM1.5 spectrum (1000 W m^{-2}) is 36%, which has been attained III–V semiconductors with lattice-mismatched materials, such as three-layer InGaP/GaAs/InGaAs solar cells (Green et al. 2012). In this way, for further improvement of solar cell efficiency, lattice-mismatched hetero-junction growth is needed. However, it is difficult to obtain good quality layer growth without generating misfit dislocations. To address this problem, we propose four-junction NW solar cells (see Fig. 5) to attain efficiency of over 50%. We have previously reported the successful growth of hetero-junction NW cells with 2.1% lattice mismatched. In the proposed four-junction cells, each NW segment has 1.1–2.3% lattice mismatched at the hetero-junction interface area. Theoretical calculation suggests that if the NW diameter in these

cells were less than 200 nm, coherent growth could be obtained without misfit dislocation formation (Glas 2006). The efficiency for cells of this type has been theoretically calculated at 55.3% (Bremner et al. 2007).

SUMMARY

We have demonstrated the use of SA-MOVPE to achieve position-controlled growth of III–V NWs for solar cell applications. The several advantages of NW solar cells make them very promising next-generation solar cells. In photovoltaic applications a periodic NW array structure has the potential to improve optical absorption while reducing optical reflections. Further, it is predicted that CS structures with radial p–n junction, which are aligned parallel to incident light, will improve the collection efficiency of photo-generated electrons and holes across the junction area. We obtained efficiency of 4.23% for InP CS NW solar cells. Moreover, the NW array structure has the advantage of saving natural resources over conventional thin film photovoltaic devices. We also formed a ‘flexible NW array’ without a substrate, thus enabling the substrate

Fig. 5 Schematic view of multi-junction NW solar cell

to be reproducibly used. This array requires two orders less of semiconductor materials for electric power generation. In addition, we proposed the use of four-junction NW solar cells to achieve over 50% efficiency. A number of issues, however, remain to be addressed to improve NW solar cells so that they can be put to practical use.

Acknowledgments The authors would like to thank Profs. Junichi Motohisa, Shinjiro Hara, and Kenji Hiruma, as well as Mr. Hajime Goto, for their fruitful discussions.

REFERENCES

- Björk, M.T., B.J. Ohlsson, T. Sass, A.I. Persson, C. Thelander, M.H. Magnusson, K. Deppert, L.R. Wallenberg, et al. 2002. One-dimensional heterostructures in semiconductor nanowhiskers. *Applied Physics Letters* 80: 1058–1060.
- Borgström, M.T., J. Wallentin, M. Heurlin, S. Fält, P. Wickert, J. Leene, M.H. Magnusson, K. Deppert, et al. 2011. Nanowires with promise for photovoltaics. *IEEE Journal of Selected Topics in Quantum Electronics* 17: 1051–1061.
- Bremner, S.P., M.Y. Levy, and C. Honsberg. 2007. Analysis of tandem solar cell efficiencies under AM1.5G Spectrum using a rapid flux calculation method. *Progress in Photovoltaics: Research and Applications* 16: 225–233.
- Colombo, C., M. Heib, M. Grätzel, and A.F.I. Morral. 2009. Gallium arsenide p–i–n radial structures for photovoltaic applications. *Applied Physics Letters* 94: 173108-1-3.
- Czaban, J.A., D.A. Thompson, and R.R. LaPierre. 2009. GaAs core–shell nanowires for photovoltaic applications. *Nanoletters* 9: 148–154.
- Fukui, T., S. Ando, and Y.K. Fukai. 1990. Lateral quantum well wires fabricated by selective metalorganic chemical vapor deposition. *Applied Physics Letters* 57: 1209–1211.
- Glas, F. 2006. Critical dimensions for the plastic relaxation of strained axial heterostructures in free-standing nanowires. *Physical Review B* 74: 121302 (4 pp).
- Goto, H., K. Nosaki, K. Tomioka, S. Hara, K. Hiruma, J. Motohisa, and T. Fukui. 2009. Growth of core–shell InP nanowires for photovoltaic application by selective-area metal organic vapor phase epitaxy. *Applied Physics Express* 2: 035004 (3 pp).
- Green, M.A., K. Emery, Y. Hishikawa, W. Warta, and E.D. Dunlop. 2012. Solar cell efficiency tables (version 39). *Progress in Photovoltaics: Research and Applications* 20: 12–20.
- Gudiksen, M.S., L.J. Lauhon, J. Wang, D.C. Smith, and C.M. Lieber. 2002. Growth of nanowire superlattice structures for nanoscale photonics and electronics. *Nature* 415: 617–620.
- Hiruma, K., T. Katsuyama, K. Ogawa, M. Koguchi, H. Kakibayashi, and G.P. Morgan. 1991. Quantum size microcrystals grown using organometallic vapor phase epitaxy. *Applied Physics Letters* 59: 431–433.
- Hiruma, K., M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, and H. Kakibayashi. 1995. Growth and optical properties of nanometer-scale GaAs and InAs whiskers. *Journal of Applied Physics* 77: 447–462.
- Hu, L., and G. Chen. 2007. Analysis of optical absorption in silicon nanowire arrays for photovoltaic applications. *Nano Letters* 7: 3249–3252.
- Kelzenberg, M.D., D.B. Turner-Evans, B.M. Kayes, M.A. Filler, M.C. Putnam, N.S. Lewis, and H.A. Atwater. 2008. Photovoltaic

- measurements in single-nanowire silicon solar cells. *Nano Letters* 8: 710–714.
- Mohan, P., J. Motohisa, and T. Fukui. 2005. Controlled growth of highly uniform, axial/radial direction-defined, individually addressable InP nanowire arrays. *Nanotechnology* 16: 2903–2907.
- Morral, A.F.I., C. Colombo, G. Abstreiter, J. Arbiol, and J.R. Morante. 2008. Nucleation mechanism of gallium-assisted molecular beam epitaxy growth of gallium arsenide nanowires. *Applied Physics Letters* 92: 063112 (3 pp).
- Noborisaka, J., J. Motohisa, and T. Fukui. 2005. Catalyst-free growth of GaAs nanowires by selective-area metalorganic vapor-phase epitaxy. *Applied Physics Letters* 86: 213102 (3 pp).
- Sugo, M., A. Yamamoto, M. Yamaguchi, and C. Uemura. 1985. High-efficiency InP solar cells with n^+p-p^+ structure grown by metal–organic chemical vapor deposition. *Japanese Journal of Applied Physics* 24: 1243–1244.
- Tian, B., X. Zheng, T.J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang, and C.M. Lieber. 2007. Coaxial silicon nanowires as solar cells and nanoelectronic power sources. *Nature* 449: 885–890.
- Wagner, R.S., and W.C. Ellis. 1964. Vapor–liquid–solid mechanism of single crystal growth. *Applied Physics Letters* 4: 89–90.

AUTHOR BIOGRAPHIES

Takashi Fukui (✉) is a professor at the Graduate School of Information Science and Technology and Director of the Research Center for Integrated Quantum Electronics at Hokkaido University.

Address: Graduate School of Information Science and Technology, Hokkaido University, N14, W9, Sapporo 060-0814, Japan.
e-mail: fukui@rciqe.hokudai.ac.jp

Masatoshi Yoshimura is a PhD student at the Graduate School of Information Science and Technology of Hokkaido University.
Address: Graduate School of Information Science and Technology, Hokkaido University, N14, W9, Sapporo 060-0814, Japan.
e-mail: yoshimura@rciqe.hokudai.ac.jp

Eiji Nakai is a Master Course student at the Graduate School of Information Science and Technology of Hokkaido University.
Address: Graduate School of Information Science and Technology, Hokkaido University, N14, W9, Sapporo 060-0814, Japan.
e-mail: nakai@rciqe.hokudai.ac.jp

Katsuhiko Tomioka is a researcher for the Japan Science and Technology Agency (JST)-PRESTO Program and for the Graduate School of Information Science and Technology at Hokkaido University.
Address: Graduate School of Information Science and Technology, Hokkaido University, N14, W9, Sapporo 060-0814, Japan.
e-mail: tomioka@rciqe.hokudai.ac.jp