Ultra-High Efficiency Photovoltaic Cells for Large Scale Solar Power Generation

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Abstract The primary targets of our project are to drastically improve the photovoltaic conversion efficiency and to develop new energy storage and delivery technologies. Our approach to obtain an efficiency over 40% starts from the improvement of III–V multi-junction solar cells by introducing a novel material for each cell realizing an ideal combination of bandgaps and lattice-matching. Further improvement incorporates quantum structures such as stacked quantum wells and quantum dots, which allow higher degree of freedom in the design of the bandgap and the lattice strain. Highly controlled arrangement of either quantum dots or quantum wells permits the coupling of the wavefunctions, and thus forms intermediate bands in the bandgap of a host material, which allows multiple photon absorption theoretically leading to a conversion efficiency exceeding 50%. In addition to such improvements, microfabrication technology for the integrated high-efficiency cells and the development of novel material systems that realizes high efficiency and low cost at the same time are investigated.

Keywords Multi-junction · Quantum well · Concentrator · Photovoltaic

INTRODUCTION

Large-scale photovoltaic (PV) power generation systems, that achieve an ultra-high efficiency of 40% or higher under high concentration, are in the spotlight as a new technology to ease drastically the energy problems. Multiple junction (or tandem) solar cells that use epitaxial crystals of III–V compound semiconductors take on the active role for photoelectric energy conversion in such PV power generation systems. Because these solar cells

operate under a sunlight concentration of $500\times$ to $1000\times$, the cost of cells that use the epitaxial crystal does not pose much of a problem. In concentrator PV, the increased cost for a cell is compensated by less costly focusing optics. The photons shining down on earth from the sun have a wide range of energy distribution, from the visible region to the infrared region, as shown in Fig. 1. Multi-junction solar cells, which are laminated with multilayers of p–n junctions configured by using materials with different band gaps, show promise in absorbing as much of these photons as possible, and converting the photon energy into electricity with minimum loss to obtain high voltage. Among the various types of multi-junction solar cells, indium gallium phosphide (InGaP)/gallium arsenide (GaAs)/germanium (Ge) triple-junction cells that make full use of the relationship between band gaps and diverse lattice constants offered by compound semiconductors have the advantage of high conversion efficiency because of their high-quality single crystal with a uniform-size crystal lattice. So far, a conversion efficiency exceeding 41% under conditions where sunlight is concentrated to an intensity of approximately $500\times$ has been reported.

The tunnel junction with a function equivalent to electrodes is inserted between different materials. The positive holes accumulated in the p layer and the electrons in the adjacent n layer will be recombined and eliminated in the tunnel junction. Therefore, three p–n junctions consisting of InGaP, GaAs, and Ge will become connected in series. The upper limit of the electric current is set by the minimum value of photon flux absorbed by a single cell. On the other hand, the sum of voltages of three cells make up the voltage.

As shown in Fig. 1, photons that can be captured in the GaAs middle cell have a small flux because of the band gap of each material. As a result, the electric current output

Fig. 1 Solar spectrum radiated on earth and photon flux collected by the *top cell* (InGaP), *middle cell* (GaAs), and *bottom cell* (Ge) (equivalent to the area of the filled portions in the figure)

from the GaAs cell theoretically becomes smaller than that of the others and determines the electric current output of the entire tandem cell. To develop a higher efficiency tandem cell, it is necessary to use a material with a band gap narrower than that of GaAs for the middle cell.

In order to obtain maximum conversion efficiency for triple-junction solar cells, it is essential to narrow down the middle cell band gap to 1.2 eV and increase the short-circuit current density by 2 mA/cm² compared with that of the GaAs middle cell. When the material is replaced with a narrower band gap, the output voltage will drop. However, the effect of improving the electric current balance outperforms this drop in output voltage and boosts the efficiency of the entire multi-junction cell.

When a crystal with such a narrow band gap is grown on a Ge base material, lattice relaxation will occur in the middle of epitaxial crystal growth because the lattice constants of narrower band-gap materials are larger than that of Ge (as shown in Fig. 2). As a result, the carrier transport properties will degrade due to dislocation.

Researchers from the international research center Solar Quest, the University of Tokyo, aim to move beyond such material-related restrictions, and obtain materials and structures that have effective narrow band gaps while maintaining lattice matching with Ge or GaAs. To achieve this goal, we have taken three approaches as indicated in Fig. 3. These approaches are explained in detail below.

DILUTE NITROGEN-ADDED BULK CRYSTAL

Indium gallium nitride arsenide (InGaNaAs) is a bulk material consists of InGaAs, which contains several percent of nitrogen. InGaNaAs has a high potential for achieving a narrow band gap while maintaining lattice matching with Ge or GaAs. However, InGaNaAs has a fatal problem, that is, a drop in carrier mobility due to inhomogeneous

distribution of nitrogen (N). To achieve homogeneous solid solution of N in crystal, we have applied atomic hydrogen irradiation in the film formation process and addition of a very small amount of antimony (Sb) (Fig. 3).

The atomic hydrogen irradiation technology and the nitrogen radical irradiation technology for incorporating N efficiently into the crystal can be achieved only through molecular beam epitaxy (MBE), which is used to fabricate films under high vacuum conditions. (Nitrogen radical irradiation is a technology that irradiates the surface of a growing crystal with nitrogen atoms that are resolved by passing nitrogen through a plasma device attached to the MBE system.) Therefore, high-quality InGaNaAs has been obtained only by MBE until now. Furthermore, as a small amount of Sb is also incorporated in a crystal, it is necessary to control the composition of five elements in the crystal with a high degree of accuracy to achieve lattice matching with Ge or GaAs.

We have overcome this difficulty by optimizing the crystal growth conditions with high precision and developed a cell that has an InGaNaAs absorption layer formed on a GaAs substrate. The short-circuit current has increased by 9.6 mA/cm² for this cell, compared with a GaAs single-junction cell, by narrowing the band gap down to 1.0 eV. This technology can be implemented not only for triple-junction cells, but also for higher efficiency lattice-matched quadruple-junction cells on a Ge substrate.

In order to avoid the difficulty of adjusting the composition of five elements in a crystal, we are also taking an approach of using GaNaAs with a lattice smaller than that of Ge or GaAs for the absorption layer and inserting InAs with a large lattice in dot form to compensate for the crystal's tensile strain. To make a solid solution of N uniformly in GaNaAs, we use the MBE method for crystal growth and the atomic hydrogen irradiation as in the case of InGaNaAs. We also believe that using 3D-shaped InAs dots can effectively compensate for the tensile strain that

Fig. 2 Relationship between band gaps and lattice constants of III–V-based and IV-based crystals

occurs in GaNAs. We have measured the characteristics of a single-junction cell formed on a GaAs substrate by using a GaNAs absorption layer with InAs dots inserted.

Figure 4 shows that we were able to succeed in enhancing the external quantum efficiency in the long-wavelength region (corresponding to the GaNAs absorption) to a level equal to GaAs. This was done by extending the absorption edge to a longer wavelength of 1200 nm, and increasing the thickness of the GaNAs layer by increasing the number of laminated InAs quantum dot layers. This high quantum efficiency clearly indicates that GaNAs with InAs dots inserted has the satisfactory quality for middle cell material (Oshima et al. 2010).

STRAIN-COMPENSATED QUANTUM WELL STRUCTURE

It is extremely difficult to develop a narrow band-gap material that can maintain lattice matching with Ge or

GaAs unless dilute nitrogen-based materials mentioned earlier are used. As shown in Fig. 2, the conventionally used material InGaAs has a narrower band gap and a larger lattice constant than GaAs. Therefore, it is difficult to grow InGaAs with a thickness larger than the critical film thickness on GaAs without causing lattice relaxation. However, the total film thickness of InGaAs can be increased as an InGaAs/GaAsP strain-compensated multilayer structure by laminating InGaAs with a thickness less than the critical film thickness in combination with GaAsP that is based on GaAs as well, but has a small lattice constant, and bringing the average strain close to zero (Fig. 3.).

This InGaAs/GaAsP strain-compensated multilayer structure will form a quantum well-type potential as shown in Fig. 5. The narrow band-gap InGaAs layer absorbs the long-wavelength photons to generate electron–hole pairs. When these electron–hole pairs go over the potential barrier of the GaAsP layer due to thermal excitation, the electrons and holes are separated by a built-in electric field

Fig. 3 Materials and structures of narrow band-gap middle cells being researched by this team

Fig. 4 Spectral quantum efficiency of GaAs single-junction cell using GaNAs bulk crystal layer (inserted with InAs dots) as the absorption layer: Since the InAs dot layer and the GaNAs bulk layer are stacked alternately, the total thickness of GaNAs layers increases as the number of stacked InAs dot layers is increased. The *solid line* in the *graph* indicates the data of a reference cell that uses GaAs for its absorption layer (Oshima et al. 2010)

to generate photocurrent. There is a high probability of recombination of electron-hole pairs that remain in the well. To avoid this recombination, it is necessary to take

out the electron-hole pairs efficiently from the well and transfer them to n-type and p-type regions without allowing them to be recaptured into the well. Designing the quantum

Fig. 5 Distribution of potential formed by the InGaAs/GaAsP strain-compensated multilayer structure: the narrow band-gap InGaAs layer is sandwiched between wide band-gap GaAsP layers and, as a result, it as quantum well-type potential distribution. In the well, electron–hole pairs are formed by absorption of long-wavelength photons and at the same time, recombination of electrons and holes takes place. The team from Solar Quest is focusing on developing a superlattice structure with the thinnest GaAsP barrier layer

well structure suited for this purpose is essential for improving conversion efficiency.

The high-quality crystal growth by means of the metal-organic vapor phase epitaxy (MOVPE) method with excellent ability for mass production has already been applied for InGaAs and GaAsP layers in semiconductor optical device applications. Therefore, it is technologically quite possible to incorporate the InGaAs/GaAsP quantum well structure into multi-junction solar cells that are manufactured at present, only if highly accurate strain compensation can be achieved.

As the most basic approach related to quantum well structure design, we are working on fabrication of superlattice cells with the aim of achieving higher efficiency by making the GaAsP barrier layer as thin as possible, and enabling carriers to move among wells by means of the tunnel effect. Figure 6 shows the spectral quantum efficiency of a superlattice cell. In this example, the thickness of the GaAsP barrier layer is 5 nm, which is not thin enough for proper demonstration of the tunnel effect. When the quantum efficiency in the wavelength range (860–960 nm) that corresponds to absorption of the quantum well is compared between a cell, which has a conventionally used barrier layer and a thickness of 10 nm or more, and a superlattice cell, which has the same total layer thickness of InGaAs, the superlattice cell demonstrates double or higher quantum efficiency. This result indicates that carrier mobility across quantum wells is promoted by even the partial use of the tunnel effect. By increasing the P composition in the GaAsP layer, the thickness of well (or the In composition) can be increased, and the barrier layer thickness can be reduced while strain compensation is maintained. A cell with higher quantum efficiency can be

fabricated while extending the absorption edge to the long-wavelength side (Wang et al. 2010, 2012).

GROWTH TECHNIQUE FOR STRAIN-COMPENSATED QUANTUM WELL

To reduce the strain accumulated in the InGaAs/GaAsP multilayer structure as close to zero as possible, it is necessary to control the thickness and atomic content of each layer with high accuracy. The In composition and thickness of the InGaAs layer has a direct effect on the absorption edge wavelength and the GaAsP layer must be thinned to a satisfactory extent to demonstrate fully the tunnel effect of the barrier layer. Therefore, it is desirable that the average strain of the entire structure is adjusted mainly by the P composition of the GaAsP layer.

Meanwhile, for MOVPE, there exists a nonlinear relationship between the P composition of the crystal layer and the P ratio $[P/(P + As)]$ in the vapor phase precursors, which arises from different absorption and desorption phenomena on the surface. As a result, it is not easy to control the P composition of the crystal layer. To break through such a difficulty and promote efficient optimization of crystal growth conditions, we have applied a mechanism to evaluate the strain of the crystal layer during growth in real time by sequentially measuring the curvature of wafers during growth with an incident laser beam from the observation window of the reactor.

As shown in Fig. 7, the wafer curvature during the growth of an InGaAs/GaAsP multilayer structure indicates a periodic behavior. Based on a simple mechanical model, it has become clear that the time changes of wafer

Fig. 6 Spectral quantum efficiency of GaAs single-junction cell using InGaAs/GaAsP superlattice as the absorption layer: This structure consists of 60 layers of InGaAs quantum wells. The graph also shows data of a reference cell that uses GaAs for its absorption layer (Wang et al. 2010, 2012)

Fig. 7 Changes in wafer curvature over time during growth of the InGaAs/GaAsP multilayer structure. This graph indicates the measurement result and the simulation result of the curvature based on the layer structure (composition + thickness) obtained by X-ray diffraction. Since compressive strain is applied during InGaAs growth, the curvature decreases as time passes. On the other hand, since tensile strain is applied during GaAsP growth, the curvature changes in the opposite direction (Sugiyama et al. 2011)

curvature are proportionate to the strain of the crystal layer relative to a substrate during the growing process. One vibration cycle of the curvature is same as the growth time of an InGaAs and GaAsP pair (Sugiyama et al. 2011).

Therefore, the observed vibration of the wafer curvature reflects the accumulation of the compression strain that occurs during InGaAs growth and the release of the strain that occurs during GaAsP growth. When the strain is completely compensated, the growth of the InGaAs/GaAsP

pair will cause this strain to return to the initial value and the wafer curvature will vibrate with the horizontal line as the center. As shown in Fig. 7, strain can be compensated almost completely by adjusting the layer structure. Only by conducting a limited number of test runs, the use of such real-time observation technology of the growth layer enables setting the growth conditions for fabricating the layer structure for which strain has been compensated with high accuracy.

FUTURE DIRECTIONS

In order to improve the conversion efficiency by enhancing the current matching of multi-junction solar cells using III–V compound semiconductors, there is an urgent need to create semiconductor materials or structures that can maintain lattice matching with Ge or GaAs, and have a band gap of 1.2 eV. As for InGaAs, which consists of InGaAs with several percent of nitrogen added, we have the prospect of extending the band edge to 1.0 eV while retaining sufficient carrier mobility for solar cells by means of atomic hydrogen irradiation and application of a small quantity of Sb during the growth process.

In addition, as for GaNAs bulk crystal containing InAs dots, we were able to extend the band edge to 1.2 eV and produce a high-quality crystal with enough film thickness to achieve the quantum efficiency equivalent to that of GaAs. These crystals are grown by means of MBE. Therefore, measures that can be used to apply these crystals for mass production, such as migration to MOVPE, will be investigated after demonstrating their high efficiency by embedding these crystals into multi-junction cells.

As for the InGaAs/GaAsP strain-compensated quantum well that can be grown using MOVPE, we are working on the development of a thinner barrier layer while compensating for the strain with high accuracy by real-time observation of the wafer curvature. We have had the prospect of achieving a quantum efficiency that will surpass existing quantum well solar cells by promoting the carrier transfer within the multilayer quantum well structure using the tunnel effect. As this technology can be

transferred quite easily to the existing multi-junction solar cell fabrication process, we strongly believe that this technology can significantly contribute to the efficiency improvement of the latest multi-junction solar cells.

REFERENCES

- Oshima, R., A. Takata, Y. Shoji, K. Akahane, and Y. Okada. 2010. InAs/GaNAs strain-compensated quantum dots stacked up to 50 layers for use in high-efficiency solar cell. *Physica E* 42: 2757–2760.
- Sugiyama, M., K. Sugita, Y. Wang, and Y. Nakano. 2011. In situ curvature monitoring for metalorganic vapor phase epitaxy of strain-balanced stacks of InGaAs/GaAsP multiple quantum wells. *Journal of Crystal Growth* 315: 1–4.
- Wang, Y., Y. Wen, K. Watanabe, M. Sugiyama, and Y. Nakano. 2010. InGaAs/GaAsP strain-compensated superlattice solar cell for enhanced spectral response. In *Proceedings 35th IEEE photovoltaic specialists conference*, 3383–3385.
- Wang, Y.P., S. Ma, M. Sugiyama, and Y. Nakano. 2012. Management of highly-strained heterointerface in InGaAs/GaAsP strain-balanced superlattice for photovoltaic application. *Journal of Crystal Growth*. doi:10.1016/j.jcrysgro.2011.12.049.

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