Progress in large area organometallic vapor phase epitaxy for III-V multijunction photovoltaics

C. M. Fetzer*, X.Q. Liu, J. Chang, W. Hong, A. Palmer, D. Bhusari, B. Jun, M. Lau, and H. Lee
Boeing-Spectrolab, Sylmar, CA, 91342, USA.

A R T I C L E I N F O

Keywords:
Germanium
Multijunction solar cells
Photovoltaics
Metamorphic
OMVPE

A B S T R A C T

Multijunction solar cells are fabricated using organometallic vapor phase epitaxy (OMVPE) to deposit subcells of GaInP and GaInAs on 150 mm diameter Ge substrates. We review the general challenges of achieving solar cell epitaxial growth on 150 mm dia. Ge and discuss basic GaInP material characterization. Metamorphic GaInP/GaInAs/Ge C4MJ epitaxial layers are characterized by in-situ curvature measurements during growth, a 99.5% relaxation by high resolution X-ray diffraction reciprocal space mapping, and a threading dislocation density in active regions of the device of 1.3 x 10^5 cm^{-2} by cathodoluminescence. Test batches of 20kWp of cells, 1.0 cm^2 in aperture area, are grown and fabricated on 100 mm and 150 mm dia. Ge wafers and average 40.2% and 40.1% efficiency, respectively, under 50 W/cm^2 AM1.D illuminated current-voltage (LIV) testing. Finally, we demonstrate very large area , >72 cm^2, triple junction XTJ space devices, averaging 29.3% efficiency for 73 such devices under space LIV testing (0.1353 mW/cm^2, 28^0C, AM0).

1. Introduction

It has been 34 years since the first publication of III-V solar cell made from layers grown by Organometallic Vapor Phase Epitaxy (OMVPE).[1] A single 0.29 cm^2 AlGaAs/GaAs heterojunction device on GaAs substrate demonstrated the power of the OMVPE technique to make high quality epitaxial semiconducting layers needed for photovoltaic devices. OMVPE and solar cells took another large step in 1985 with the development of the GaInP/GaAs dual junction tandem device reaching 27.3% efficiency.[2,3] Today, III-V multijunction devices dominate the world record efficiency tables for both un-concentrated and concentrated illumination.[4] The availability of very high quality lattice matched and mismatched alloys in the III-V alloy system enable a host of varying device configurations.[5-7] The triple-junction (3J) GaInP/GaAs/Ge based solar cell is now the standard in space applications.[8] And similarly, 3J GaInP/GaAs/Ge devices adapted for high illumination concentrated photovoltaic (CPV) application have begun to be applied in some terrestrial power applications.[9]

Two standard 3J device designs epitaxial cross-sections are shown in figure 1. A lattice matched GaInP/GaAs/Ge triple junction in figure 1(a) details the multiple GaInP and GaAs subcell layers interconnected with highly-doped, thin tunnel junction. A second variant, an upright metamorphic GaInP/GaInAs/Ge device is shown in figure 1(b). The main difference between the two is the use of a GaInAs graded buffer layer to change lattice constant from the Ge substrate to a new compressive lattice constant. The buffer layer also serves to relax the mismatch between the two trapping dislocations away from the active regions of the device. Details on each device and their epitaxial characterization have been detailed in previous work.[9]

The III-V multijunction device still only represents a small fraction of the overall terrestrial photovoltaic (PV) business. The challenge to III-V CPV is to deliver that high efficiency at a lower Levelized Cost of Energy (LCOE). Fortunately, there are many ways CPV can drive down LCOE. Some examples include: large-scale volume production, a concomitant drop in raw material costs, higher cell efficiencies and improved device structures. All of these directions are worth investigation. And many new results are being reported regularly in particular on novel device designs.[10, 11]

In this paper, we focus on using OMVPE on large area Ge wafers to implement reduced cell costs, taking an industrial perspective on OMVPE of CPV and Space PV devices. We discuss basic challenges of epitaxial growth on 150 mm

*Principal corresponding author. Tel.: 1-818-898-2893
E-mail address: christopher.m.fetzer@boeing.com (Chris Fetzer)

diameter (dia.) vicinal (001) Ge wafers. Then, we apply that basic growth a single CPV device structure, the metamorphic 40% efficient C4MJ tested at 550x concentration (50 W/cm^2, 25^{0}C, AM1.5D ASTM G173-03). Finally, we show results on applying OMVPE to enable the largest single die epitaxial device made to date by OMVPE, a 29% efficient greater than 72 cm^2 space solar cells at 1-sun space illumination (0.1353 mW/cm^2, 28^{0}C, AM0).

2. Experimental

All epitaxial semiconductor layers were grown by OMVPE in a commercial Veeco K475 large-scale reactor. This tool is capable of 15 x 4" (100 mm dia.) or 7 x 6" (150 mm dia.) wafers in a single epitaxial growth run. The process used industry standard growth techniques, temperatures, precursor gases and liquid organometallic sources. The reactor was operated at reduced pressure under standard growth conditions for GaInP, GaInAs and similar alloys. Growths were conducted on p-type, epi-ready vicinal (001) Ge of either 100 mm or 150 mm in diameter. The substrates used in this report are between 175 μm and 235 μm in thickness. In-situ curvature measurements were made using a Veeco combined RealTemp emissivity corrected pyrometer and Deflectometer (or DRT) head located on a top viewport of the reactor targeted at the center-point of the 150 mm outer ring of wafers.

Post growth epitaxial layer characterization was performed using white light reflectance and room-temperature photoluminescence (PL) in a Nanometrics RPM2000 with either: a white light halogen lamp, a 785 nm diode laser or a 532 nm Nd:YAG laser as the excitation source. Rocking curves are either (004) symmetric or (115) glancing exit scans or reciprocal space maps of high resolution X-ray diffraction (HRXRD) were performed on either a Bruker D8 or a Philips MRD system operated in triple-axis mode using CuKα_1 X-ray source. Threading dislocation density was evaluated using cathodoluminescence (CL) by plan-view SEM at NREL as a service by Dr. Manuel Romero with electron beam accelerated at 15keV and 500 pA beam current.

Final devices were anti-reflection coated and fabricated using standard Spectrolab methods and production process lines. Illuminated current-voltage (LIV) characteristics were taken on all devices. CPV devices were tested using pulsed illumination at 50 W/cm^2 (25^{0}C, AM1.5D ASTM G173-03). The simulator spectrum was calibrated using balloon traceable standard reference cells. Space cells were tested using a Spectrolab X-25 solar simulator at 0.1353 W/cm^2 (28^{0}C, AM0) calibrated using cells traceable to NASA Learjet flown XTJ component cell standards.

3. Basic Epitaxial Growth

Before launching into growth of III-V layers on large diameter Ge it is helpful to provide some context for difficulties unique to this type of materials system. Epitaxial growth on Ge wafers has been under active investigation for a long time.[12- 14] Scaling the size of the substrate must take into account all of those previously studied complexities. Two quick examples of those challenges are anti-phase domain formation and auto-doping of the Ge in the III-V layers. Another complexity is the thickness of the substrate. Commercial Ge wafers are significantly thinner than GaAs or InP substrates of the same diameter with typical 100 mm dia. Ge wafers ranging from 140 μm to 175 μm thick. Such relatively thin wafers amplify in-situ wafer bow during growth from lattice mismatched layers. Any wafer bow translates into non-uniform temperature across the wafer growth surface. Therefore, scaling a process to larger diameter Ge wafers makes compositional uniformity of temperature sensitive alloy a significant growth a challenge.

Perhaps the best demonstration of process suitability for growth on 150 mm dia. Ge wafers is to begin by characterizing simple alloy layers. Test layers of nearly lattice-matched 1.0 μm $Ga_{0.5}In_{0.5}P$ (herein GaInP) were grown on suitable nucleation and GaAs buffers on 150 mm dia. (001) vicinal Ge wafers. The layers were capped with 30 nm thick $Al_{0.5}In_{0.5}P$ (herein AlInP) passivation layers to act as minority carrier windows. HRXRD (004) rocking curves of the test layers taken at 9 point cross-pattern were -270" +/- 10" compressive relative to the substrate and 100% strained. Figure 2 shows the results of PL mapping showed high compositional uniformity of the GaInP layers with a PL peak energy across the wafer of 1.882 +/- 0.003 eV with no change in composition at the edge of the wafer. Likewise, PL intensity of the layer was uniform and for the majority of the wafer with a 16.3% variation (standard deviation/average) across the wafer without an edge exclusion zone. The outer 5 mm of the wafer shows a reduction in intensity to 1/3 that of the majority of the wafer.

4. 40% Efficient Metamorphic CPV

The next step in developing 150 mm dia. Ge wafers is to evaluate a CPV product grown on them. To that end, we grew a standard C4MJ GaInP/GaInAs/Ge metamorphic solar cell structure on both 100 mm and 150 mm diameter wafers. The structure of C4MJ is similar to that shown in figure 1(b). The C4MJ structure uses a graded buffer layer to change lattice constant from the Ge to that of a $Ga_{0.95}In_{0.05}As$, or a 0.277% mismatch. The in-situ curvature measurement of the wafer during growth showed a +120 km^{-1} curvature that was established during the growth of the graded buffer layer. The curvature was maintained throughout the growth with small changes observed during gas phase switching and the growth of the thin passivation and interconnecting tunnel junction layers. A +120 km^{-1} curvature translates to a convex bow of the wafer where the center of the 150 mm wafer is separated from the graphite platter by 0.337 mm. We measured from the in-situ real-time emissivity corrected pyrometer a temperature difference of 7^{0}C between the wafer edges the center. The wafer edges are hotter since it is in good contact with the graphite. This difference adds to the growth complexity in that the GaInP and similar AlInP passivation layers temperature sensitive in composition. Similarly, the $Ga_{0.95}In_{0.05}As$ post-grade buffer, middle cell and capping layers are also compositionally sensitive to the temperature.

Given the observed in-situ bow, post growth characterization on the epitaxial layers starts with evaluating the crystal relaxation by HRXRD. Figure 3 shows a HRXRD RSM at the (115) glancing exit taken on a C4MJ epitaxial structure grown on a 150 mm dia. Ge wafer. Using the method shown in Chauveau et al. [15], we can evaluate that the middle cell and graded buffer layer is exactly 5.0% Indium and 99.5% relaxed. Structures were further characterized by plan view CL in an SEM to investigate the threading dislocation density (TDD). We find that the TDD is regional to the wafer with some regions with no dislocations observed in 100 μm x 100 μm regions. From the average of 10, 30 μm x 30 μm images, we calculate TDD for the sample to be 1.3 +/- 0.3 x 10^5 cm^{-2}. That density is a very low number for a metamorphic structure. We have demonstrated similar densities for $Ga_{0.92}In_{0.08}As$ – based metamorphic PV structures in previous studies.[9] The low TDD also indicates that despite the wafer bow, we can attain equivalent relaxation in the crystal structure on 150 mm dia. wafer growth as on 100 mm dia. wafer growth in the previous study.

Ultimately our aim is to manufacture C4MJ cells on 150 mm dia. wafers. To demonstrate the comparative capability of the process in pilot scale, two test batches of 20 kWp (~1000 cells) of C4MJ cells were made on 150 mm and 100 mm dia. wafers. Both types of wafers were grown on the same reactor at the same time with the same growth conditions. Wafers were subsequently processed into 1 cm^2 active area CDO-100 devices and tested at 50 W/cm^2 (550x concentration) as described above. Figure 4 shows the open circuit voltage (V_{oc}) uniformity averaged over all wafers and as a percentage of target value. Contrary to the observed intensity reduction in the outer 5 mm of the PL mapping, the C4MJ cells at concentrated LIV testing do not show any significant reduction in V_{oc}. The difference is the intensity of the excitation. Low-level non-radiative recombination pathways observed in PL saturate at high illumination levels experienced in CPV. Figure 5 shows a histogram of the two C4MJ test populations. Cells from both 100 mm dia. and 150 mm dia. wafers averaged above 40% efficiency at maximum power, at 40.2% and 40.1%, respectively. The highest efficiency device we tested from the batch was 42.6%. That result is not a world record device, but is very high for a production cell. Noticeably, the C4MJ fabricated on 150 mm dia. wafers showed a higher amount of variability. That variation will likely be reduced as these wafers go into larger scale production. As a final marker for the status of the development, at the time of this writing C4MJ devices from both 100 mm and 150 mm dia. wafers have been on-sun in concentrator arrays at two sites for over a year and show expected field performance gains over the lattice matched devices.[16,17]

5. 29% Efficient Very Large Devices for Space

A further return is the use of 150 mm dia. Ge wafers in space device production. Unlike CPV, space PV devices are very large in area. Spectrolab's largest commercial device is the 59.65 cm^2 XTJ, referred to as a 1-per device since only one die is made per 100 mm dia. Ge wafer.[18] Incorporating a 150 mm dia. Ge wafer in place of the 100 mm dia. wafer enables the fabrication of devices >72 cm^2 2-per (2 die per wafer) XTJ cells. We believe this demonstration is the largest single die III-V epitaxial device made to date. Growth of wafers was performed in a similar fashion to C4MJ 150 mm dia. wafer growth. In this case, a lattice matched structure, XTJ, similar to the structure in figure 1(a) was used. XTJ 2-per devices on 100 mm dia. Ge fully space qualified and nominally 29.5% efficient under AM0 spectral testing.[8]

Initially, a smaller cell test pattern of 4 cm^2 (square), 2 cm^2 (rectangular) and 2.56 cm^2 (triangular) cells were fabricated on XTJ structures grown on 150 mm dia. Ge wafers. Similar to results obtained for C4MJ wafers, highly uniform short circuit current density (J_{sc}), V_{oc}, and Fill factor were obtained for the square 4 cm^2 devices in the center of the wafer. Interestingly, the outermost cells (rectangular and triangular) show a slight drop in V_{oc} and maximum power voltage (V_{mp}). A map of the Voc for all cells by position normalized to the average is shown in figure 6. This drop near the edge does coincide with the PL intensity reduction near the edge of the wafer. Up to a 3% relative drop in V_{oc} is observed for the outermost cells. The lower illumination intensity at 1-sun (0.1353 W/cm^2) means that the non-radiative recombination of minority carriers becomes more significant in the device performance.

These results are interesting, but do not translate into the large device performance. While, the edge reduction is part of the larger device, its effects are averaged over a much larger area and are inconsequential to the overall device performance. Table 1 shows the LIV characteristics of the average population of 73 large area cells made in 4 separate processing batches in comparison to 1-per and 2-per devices from 100 mm dia. Ge wafers. The record cell tested in all the >72 cm^2 cell batches was 30.3% efficient. Figure 6 shows a histogram of the cell batches showing a nominally tight distribution of promising results in these early experimental devices. Further work will be required to bring this product to market, including a space qualification testing regimen.

6. Summary

Successful III-V solar cell growth by OMVPE on thin, 150 mm dia. Ge was conducted for basic layers, showing high compositional uniformity of GaInP test layers with peak PL energy of 1.883 +/- 0.003 eV with no edge exclusion. PL intensity for the same peak showed a reduction to 1/3 of the nominal average near 5 mm from the edge, but otherwise very uniform intensity. Basic layer examples were translated into metamorphic GaInP/GaInAs/Ge C4MJ 3J epitaxial layers with near 100% lattice relaxation despite showing 120 km-1 of wafer curvature during growth. TDD's in these layers were characterized at 1.3 +/- 0.3 x 10^5 cm^{-2}. Two test batches of C4MJ CDO-100 devices were fabricated from 150 mm and 100 mm dia. Ge wafer growths and both averaged over 40% efficiency under 550x AM1.5D pulsed illumination testing. Finally, these efforts were used to convert lattice-matched XTJ space solar cells at 30.3% efficiency under AM0 testing for a device greater than 72 cm^2 in area, the largest area epitaxial III-V device demonstrated to date.

Acknowledgments

Many people make PV and CPV happen at Spectrolab. OMVPE is only one step in the processe the manufacture photovoltaics at Spectrolab. The authors wish to thank the support of the entire multijunction team of scientists, engineers, technicians and support people that make this happen. Jeff Krogen, Richard King, Jim Ermer, Nasser Karam, S. K. Sharma, Pete Hebert, Robert Cravens, Russ Jones, Peichen Pien, Ricardo Anya, William Wise, and Mark Takahashi were particularly helpful in this present work. This work was supported by Boeing-Spectrolab.

References

[1] R. D. Dupuis, P. D. Dapkus, R. D. Yingling, and L. A. Moudy, Appl. Phys. Lett., **31** (1977) p. 201.

[2] J. M. Olson – US Patent #4,667,059 (1985).

[3] J. M. Olson, S. R. Kurtz, A. E. Kibbler and P. Faine, Appl. Phys. Lett., **56** (1990) p. 624

[4] M. A. Green, K. Emery, Y. Hishikawa, and W. Warta, Prog. Photovolt.: Res. Appl. (2011) **19** p. 84. DOI: 10.1002/pip. 1088

[5] M. Stan, D. Aiken, B. Cho, A. Cornfeld, V. Ley, P. Patel, P. Sharps, T. Varghese, J. Crystal Growth **312** (2010) p. 1370. DOI:10.1016/j.jcrysgro.2009.10.059

[6] R. R. King, D. C. Law, K. M. Edmondson, C. M. Fetzer, G. S. Kinsey, H. Yoon, R. A. Sherif, and N. H. Karam; Appl. Phys. Lett. **90** (2007) p. 183516. DOI:10.1063/1.2734507

[7] T. N. D. Tibbits, K.W.J. Barnham, J.S. Roberts, I. M. Ballard, M. Pate, M. Geen; 28th IEEE Photovoltaic Specialist Conf. (2008) p. 1. DOI: 10.1109/PVSC.2008.4922899

[8] B. Jun, C. M. Fetzer, K. Rouhani; W. G. Wise, D. Krut, K. Bui; D. Hom, C. J. Cho, J. Z. Wu, R. Anaya, R. Bardfield, D. A. Russell, P. Leung, M. Gillanders, S. K. Sharma, J. P. Hanley; 35th IEEE Photovoltaic Specialist Conf. (2010) p. 2554. DOI: 10.1109/PVSC.2010.5614561

[9] C. M. Fetzer, R. R. King, P. C. Colter, K. M. Edmondson, D. C. Law, A. P. Stavrides, H. Yoon, J. H. Ermer, M. J. Romero, N. H. Karam; J. Crystal Growth., **261** (2004) p 361. DOI:10.1016/j.jcrysgro.2003.11.026

[10] F. Dimroth, W. Guter, J. Schone, E. Welser, M. Steiner,E. Oliva, A. Wekkeli, G. Siefer, S. P. Philipps, A. W. Bett; 34th IEEE Phot. Spec. Conf. (2009) pp: 001038 - 001042 DOI:10.1109/PVSC.2009.5411199

[11] D. Weldon (April 14, 2011) Solar Junction Breaks World Record with 43.5% Efficient CPV Production Cell, press release, retrieved April 14, 2011, http://www.sjsolar.com/downloads/Solar_Junction_World Record_%20Efficiency_14April11.pdf

[12] K. Mizuguchi, N. Hayafuji, S. Ochi, T. Murotani, K. Fujikawa. J. Crystal Growth 77 (1986) p. 509.

[13] S. Tobin, S. M. Vernon, C. Bajgar, V. E. Haven Jr., S. E. Davis, 18th IEEE Photovoltaic Specialist Conf. (1985) p. 134.

[14] G. Timó, C. Flores, D. Passoni, C. Bocchi, P. Franzosi, L. Lazzarini, G. Salviati, J. Crystal Growth 125 (1992) p. 440.

[15] J. M. Chauveau, Y. Androussi, A. Lefebvre, J. Di Persio, and Y. Cordier, J. Appl. Phys., **93** (2003) p. 4219. DOI: 10.1063/1.1544074

[16] O. Al Taher, R. Cravens, P. Pien, R. Jones, J. Ermer, P. Hebert, J. Chin; 35th IEEE Photovoltaic Specialist Conf. (2010) p. 1995. DOI: 10.1109/PVSC.2010.5616489

[17] J.H. Ermer, R.K. Jones, P. Hebert, P. Pien, R.R. King, D. Bhusari, R. Brandt,O. Al-Taher, C. Fetzer, G. S. Kinsey, and N. Karam. IEEE. J. Photovoltaics, In Press.

[18] R. Bardfield, S. K. Sharma, D. Peterson, B. Jun, J. Hanley, 37th IEEE Photovoltaics Specialist Conf. In Press.