Improving GaP Solar Cell Performance by Passivating the Surface Using AlxGa1–xP Epi-Layer

Xuesong Lu, *Member, IEEE,* Ruiying Hao, Martin Diaz, Robert L. Opila, and Allen Barnett, *Member, IEEE*

***Abstract*—A good candidate for the top junction cell in a multi-junction solar cell system is the GaP solar cell because of its proper wide band gap. Here, for the first time, we passivate the front surface of these GaP solar cells with an AlGaP layer. To study the passivation effect of this layer, we design a novel growth procedure via liquid phase epitaxy. X-Ray diffraction results show that the resulting passivation epitaxial layer is of good quality. Integrated quantum efficiency measurements show an 18% increase in current due to the AlGaP. The current–voltage measurements indicate that with this AlGaP surface passivation layer, the GaP solar cell's efficiency is 2.90%. This is an improvement over previously reported results for GaP solar cells.**

***Index Terms*—AlGaP, GaP, LPE, surface passivation**

I. INTRODUCTION

DUE to its potential for increasing the theoretical efficiency of multi-junction solar cell systems, a wide band gap solar cell is valuable [1]–[5]. Thus, the large band gap of GaP makes it a good candidate for the top junction solar cell in a 5-junction solar cell system [1], [2], [6]. However, GaP solar cells exhibit low efficiencies because they are limited by low diffusion lengths in the bulk region and high surface recombination velocities [6], [7].

Lu *et al.* [7], [8] reported a GaP solar cell with an efficiency of 2.42%. This solar cell had a GaP p–n junction grown on a p-type GaP substrate by liquid phase epitaxy (LPE). However, its high front surface recombination velocity and its low diffusion length in the emitter greatly decreased its performance. In a thin emitter it is difficult to separate low diffusion length from surface recombination. Short wavelength improvements in quantum efficiency indicate that the AlGaP has provided emitter passivation, similar to other Al containing layers for GaAs solar cells [9].

Bittner *et al.* [10] discussed GaP solar cells for space applications. Their GaP solar cells had an efficiency of 1.34% under AM 1.0. Applying five layers of InGaP quantum wells to these solar cells to increase the short circuit current density (Jsc) only increased the efficiency to 1.83% under AM 1.0. Montgomery *et al.* [11] reported that immersing bulk p-type GaP:Zn substrates in a phosphorus-saturated gallium-aluminum melt at 975 °C for 1 h significantly reduced the minority-carrier recombination centers that are associated with oxygen. However, they gave no lifetime data or solar cell efficiency data. Allen *et al.* [6] reported a GaP solar cell with 2.6% efficiency. This solar cell had a Jsc of 1.81 mA/cm^2, an open circuit voltage (Voc) of 1.48 V and a fill factor (FF) of 77%. Its epitaxial layers were grown by molecular beam epitaxy (MBE). Moreover, these researchers mentioned that one of the main limitations of quantum efficiency (QE) in the short wavelength range is high front surface recombination. Since surface passivation can reduce the surface recombination velocity, it offers an important way [6], [7] to achieve high performance GaP solar cells.

II. SURFACE PASSIVATION

Surface passivation is very important for high efficiency solar cells. The Si solar cell with the highest reported efficiency used thin thermal SiO_2 as the front surface passivation material [12]. Moreover GaAs solar cells only achieved high efficiency when AlGaAs was used as the surface passivation layer [9]. Even though surface passivation is critically important for high performance solar cells, reports on surface passivation for GaP solar cells are limited [13].

The internal quantum efficiency (IQE) simulation shown in Fig. 1 demonstrates the importance of surface passivation for GaP solar cells. In the simulation, the thicknesses of the n-type emitter and p-type base are 0.5 and 8 μm, respectively. The dopant concentrations of the emitter and base are 1×10^{18} and 1×10^{17} cm^{-3}, respectively. If the diffusion length in the emitter is 1 μm (which is longer than the emitter thickness of 0.5 μm), the IQE in the short wavelength range greatly improves as the front surface recombination velocity decreases. Thus, if this recombination velocity decreases from 1×10^6 to 1×10^3 cm/s, the IQE in the short wavelength range increases

---

Manuscript received February 4, 2013; revised April 12, 2013 and May 29, 2013; accepted May 31, 2013. Date of publication June 20, 2013; date of current version August 26, 2013. The review of this paper was arranged by Editor R. Singh.

X. Lu and M. Diaz are with the Department of Electrical and Computer Engineering, University of Delaware, Newark 19711 USA (e-mail: xslu@udel.edu; mdiaz@udel.edu).

R. Hao is with Crystal Solar, Inc., Santa Clara, CA 95130 USA (e-mail: haoruiying@gmail.com).

R. Opila is with the Department of Materials Science and Engineering, University of Delaware, Newark, NJ 19716 USA (e-mail: opila@udel.edu).

A. Barnett is with School of Photovoltaic and Renewable Energy Engineering, The University of New South Wales, Sydney 2052, Australia (e-mail: allen.barnett@unsw.edu.au).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/JEDS.2013.2266410

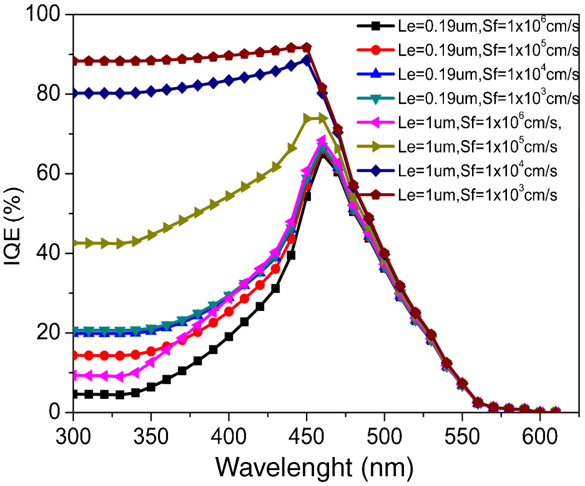


Fig. 1. Simulated IQE curves of GaP solar cells with 0.19 and 1.0 μm emitter diffusion lengths (Le) for different surface recombination velocities (Sf).

TABLE I
SIMULATED J--V CURVES PARAMETERS OF THE GAP SOLAR CELLS IN FIG. 1

Le (μm)	Lb (μm)	Sf (cm/s)	Jsc (mA/cm^2)	Voc (V)	FF (%)	η (%)
0.19	3.5	1×10^6	3.02	1.571	91.72	4.35
0.19	3.5	1×10^5	3.18	1.575	91.74	4.59
0.19	3.5	1×10^4	3.28	1.576	91.74	4.74
0.19	3.5	1×10^3	3.29	1.577	91.75	4.76
1	3.5	1×10^6	3.60	1.625	91.94	5.37
1	3.5	1×10^5	4.58	1.645	92.02	6.93
1	3.5	1×10^4	5.69	1.664	92.09	8.71
1	3.5	1×10^3	5.93	1.667	92.10	9.10

from 10% to 90%. Even with a diffusion length in the emitter of 0.19 μm (which is much shorter than the emitter thickness), as the front surface recombination velocity decreases, the IQE in the short wavelength range still increases.

For each solar cell illustrated in Fig. 1, Table 1 shows the Voc, Jsc, and efficiency. With a diffusion length in the emitter of 0.19 μm, as the front surface recombination velocity decreases from 1×10^6 to 1×10^3 cm/s, the efficiency increases from 4.35% to 4.76%. If the diffusion length in the emitter is increased to 1 μm, as the front surface recombination velocity decreases to 1×10^3 cm/s, the efficiency of the solar cell can reach over 9%. Thus, our simulation results verify that surface passivation is very important in achieving high performance GaP solar cells.

In order to serve as a good surface passivation layer for a solar cell, the material needs to exhibit three important features. First, the material must have a higher band gap than the solar cell material; otherwise, photons with the proper energy will be absorbed by the passivation layer. Second, the passivation material must have a low lattice mismatch with the solar cell material so it achieves high crystalline quality. Third, the passivation layer must be able to decrease the surface recombination velocity of the solar cell by forming an energy barrier against the minority carriers or by decreasing the density of dangling bonds at the interface.

AlGaP is a good candidate for the surface passivation layer of GaP solar cells, since it exhibits these three features. It has a tunable band gap (2.26–2.45 eV) that is higher than GaP's band gap. The lattice mismatch between GaP and AlGaP is less than 0.2%. It can form a barrier for minority carriers at the GaP/AlGaP interface. Prutskij *et al.* [13] used AlGaP layers with different Al compositions to passivate the GaP photosensor, and found that the QE of the photosensor in the short wavelength range was significantly improved by using an AlGaP passivation layer.

III. GROWTH OF ALGAP SOLAR CELL VIA LPE

Here, we successfully grew AlGaP epitaxial layers on GaP (100) substrates via liquid phase epitaxial (LPE) growth. Ga was chosen for the metal solvent because it can wet the GaP substrate and it has been proven to give good growth results by LPE [14]. The substrates were 450–500 μm thick with a doping concentration of 5×10^{16} cm^{-3} for the baseline GaP solar cell. The same GaP substrate was used as the source wafer to saturate the growth solution.

The growths took place under atmospheric pressure in the hydrogen atmosphere. During the growth, the system's temperature was first raised to 750 °C. The GaP source wafer was then moved to contact with the first solution to make it saturated with GaP. After a saturation period of 30 min, the solution was removed from the source wafer and the temperature of the solution was lowered by 2 °C to create a supersaturated state. It has been shown that the super saturation of the solution can improve the epitaxial layer's surface morphology by increasing the density of initial island formation [15]. The supersaturated solution was then brought over the seed substrate and the temperature was further lowered at the desired rate for the desired growth rate. The rates used were between 1/2 to 1 °C/min and the ΔT was from 10 to 30 °C for different layer thicknesses.

Fig. 2 shows the energy dispersive spectroscopy (EDS) results of the epitaxial layer's composition. The EDS results indicate that the composition is $Al_{0.7}Ga_{0.3}P$ and that this layer has a band gap of 2.4 eV by assuming the band gap is linearly changing as the Al composition changing. Varying the amount of Al in the Ga solution allows us to tune the composition of the AlGaP layer [16].

To analyze the crystalline quality of the epitaxial layer, we used high resolution X-ray diffraction (XRD) characterization. Fig. 3 shows that the full width at half maximum (FWHM) of the triple crystal (TC) omega scan rocking curve is 73.44 s. Equation (1) below is used to calculate the dislocation density. First, taking a radial or ω rocking curve scan of the epitaxial layer peak and estimate the dislocation density from the full width half maximum, β[17]:

$$IQE_b = \left(\frac{\beta^2}{9b^2}\right) \tag{1}$$

where b is the Burgers vector of a threading dislocation in the epitaxial material. The threading dislocation

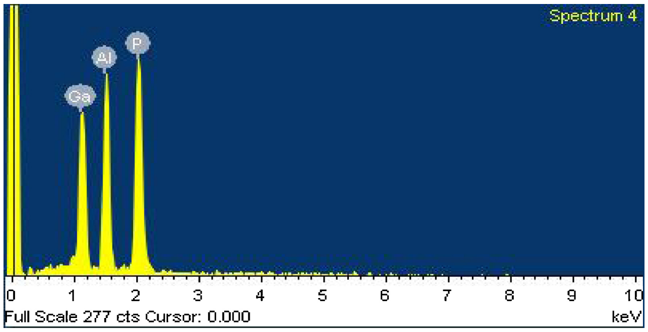


Fig. 2. EDS results for the composition of the AlGaP epitaxial layer.

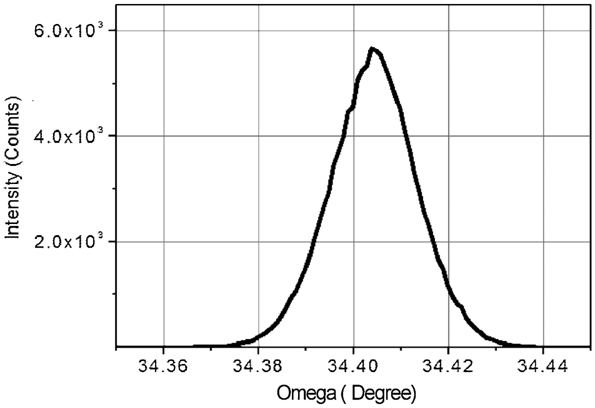


Fig. 3. XRD rocking curve TC omega scan of an AlGaP epitaxial layer on a GaP (100) substrate.

density of the growth layer is calculated to be approximately 3×10^6 cm^{-2}.

IV. GAP SOLAR CELLS FABRICATION PROCEDURE

To compare performance with and without a passivation layer, we performed the novel fabrication procedure of GaP solar cells via LPE shown in Fig. 4. LPE offers the unique advantage of fabricating two different solar cell structures on the same wafer in the same run by controlling the push rod's position during growth. This feature allows a more analytical comparison of the two structures. The back and front contacts are deposited on the sample after LPE growth. Then the sample is cut into two pieces providing two GaP solar cells, both with the same base and emitter regions, but one with an AlGaP passivation layer and one without. The thickness and the dopant concentration of the n-type GaP emitter were 0.5 μm and 1×10^{18} cm^{-3}, respectively. The thickness and the dopant concentration of the AlGaP layer were 0.15 μm and 1×10^{19} cm^{-3}, respectively.

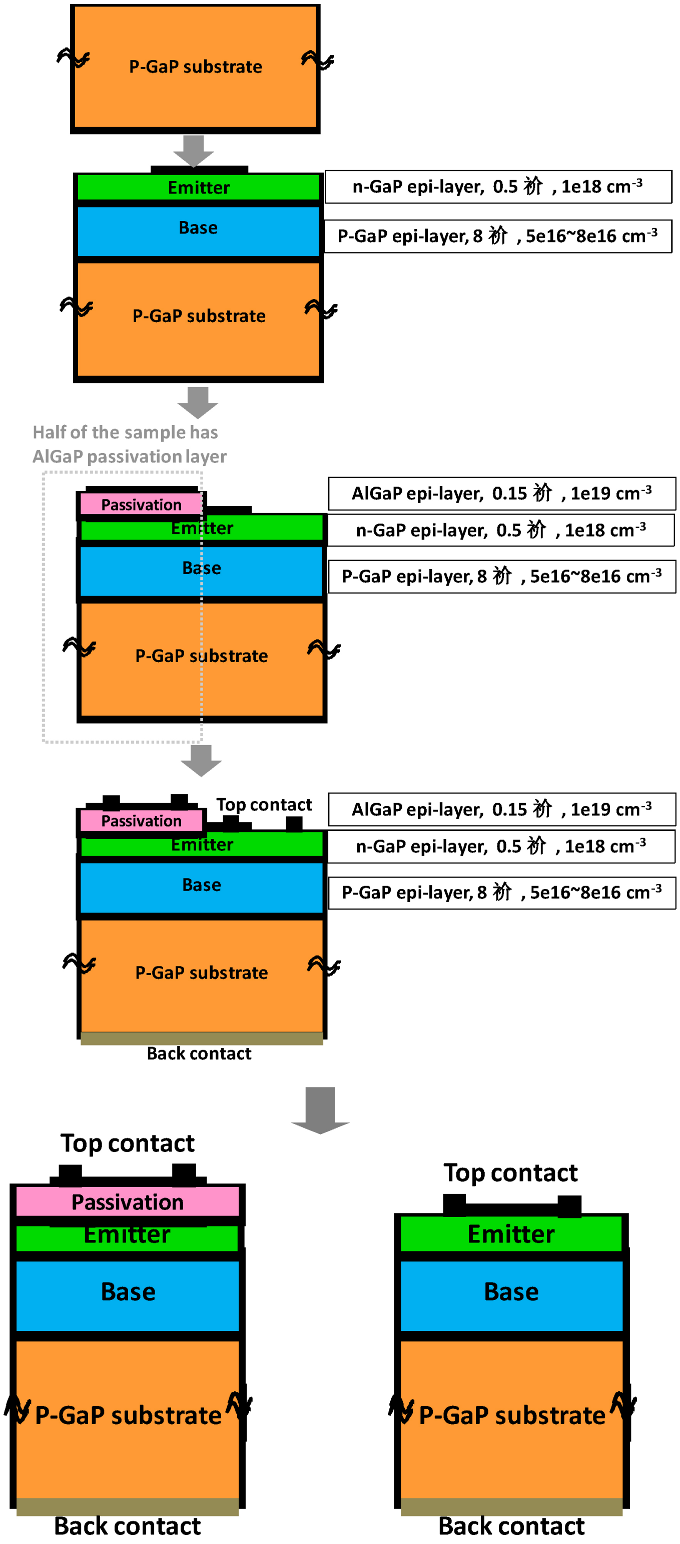


Fig. 4. Fabrication procedure in one LPE run of GaP solar cells with and without the AlGaP front surface passivation layer.

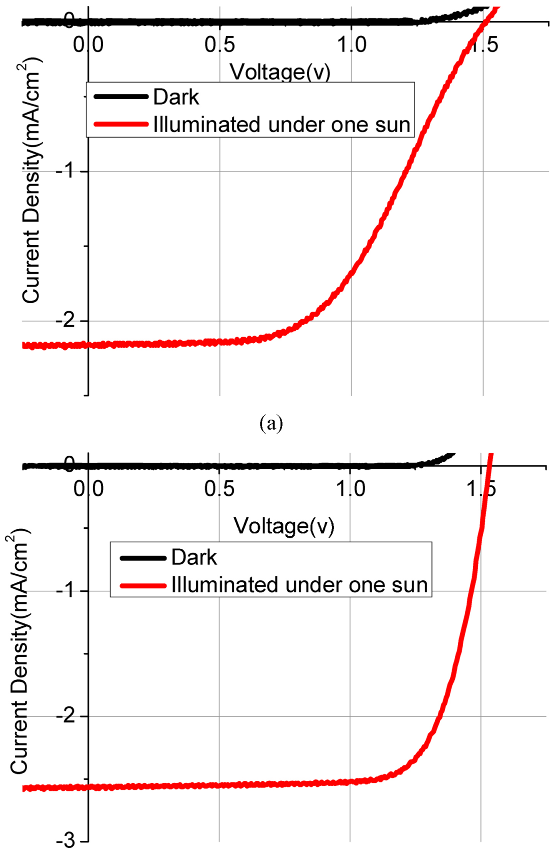
V. COMPARISON OF TWO SOLAR CELLS RESULTS

Table 2 shows the J–V curve parameters of the two GaP solar cells fabricated using the above procedure. On top of these GaP solar cells, 50 nm Si_3N_4 and 20 nm SiO_2 layers were deposited by PECVD as AR coating. The solar cell with the AlGaP front surface passivation layer displayed an efficiency of 2.90%, the highest efficiency reported for a GaP solar cell so far. Although FF was low for the cell without the AlGaP layer, a phenomenon that we will explain later, our experiment clearly shows a gain in current between the nearly identical samples.

Fig. 5 shows J–V curves for these two GaP solar cells. The solar cell measurements were made in the sunlight using a

TABLE II
J--V PARAMETERS OF GaP SOLAR CELL WITH AND WITHOUT AlGaP PASSIVATION LAYER

Solar cell	Jsc (mA/cm^2)	Voc (V)	FF (%)	η (%)
Without AlGaP	2.16	1.51	52.67	1.72
With AlGaP	2.56	1.53	74.06	2.90



(a)

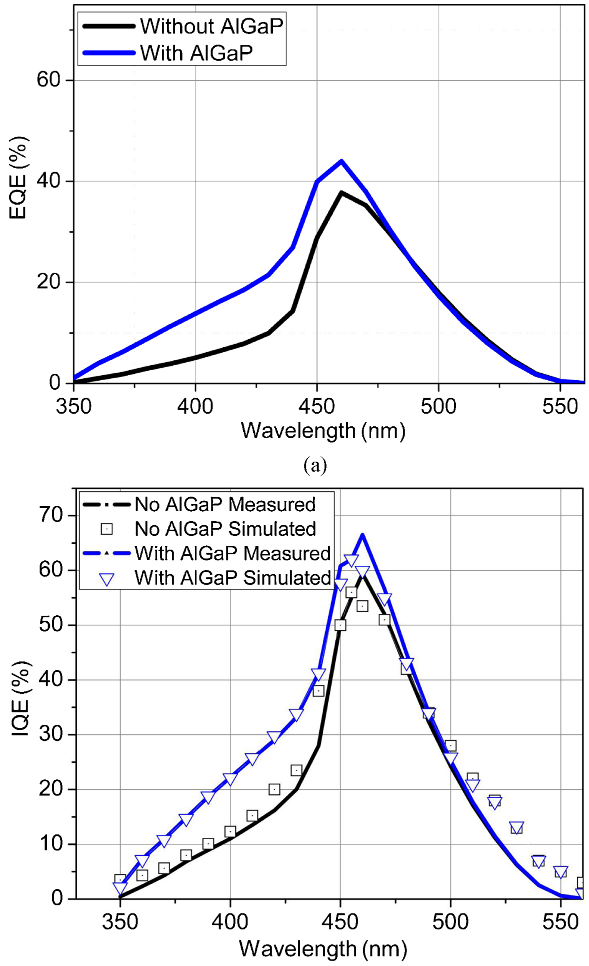
(b)

Fig. 5. J–V curves of GaP solar cells (a) without an AlGaP surface passivation layer, and (b) with it.

calibrated pyrheliometer. The detailed measurement method is described in [18].

The GaP solar cell with the AlGaP surface passivation layer achieves better performance than the one without it. The gain in Jsc is 0.4 mA/cm^2. The FF of the solar cell with the AlGaP layer is also higher since the series resistance is lower. This difference in series resistance is mainly caused by the difference in dopant concentrations of the top surface layer that directly contacts the front metal contact. The dopant concentration of AlGaP is 1×10^{19} cm^{-3}, a much higher concentration than the n-type GaP emitter's dopant concentration of 1×10^{18} cm^{-3}, thus it can form a better ohmic contact.

Fig. 6 shows the measured EQE curves and the simulated/measured IQE curves for the two GaP solar cells. The integrated current density from EQE curve indicates that the Jsc improvement of the sample with AlGaP passivation layer is mainly from short wavelength range. 0.713 mA/cm^2 for the AlGaP layer and 0.376 mA/cm^2 at the range of 350–450 nm. Based on these results, the GaP solar cell with AlGaP front surface passivation has a better QE response at short wavelengths. Since both solar cells were grown in the same run with the only difference being the AlGaP front surface passivation layer, our IQE results indicate that the AlGaP surface passivation layer decreases the front surface recombination velocity.



(a)

(b)

Fig. 6. Measured EQE curves and (b) measured and simulated IQE for GaP solar cells with and without an AlGaP front surface passivation layer.

Our simulated curve fitting verifies the recombination velocity decrease with AlGaP surface passivation layer. In our simulation, the diffusion lengths in the emitter and base regions were 0.2 and 2.3 μm, respectively. The thickness of the AlGaP layer and the diffusion length in this layer were 0.15 and 0.10 μm, respectively. The resulting front surface recombination velocity was approximately 2×10^6 cm/s for the solar cell without AlGaP front surface passivation. However, when AlGaP surface passivation was added, the surface recombination velocity decreased to 1×10^4 cm/s. The QE simulation method can be found in [8].

VI. CONCLUSION

Due to their wide band gap, GaP solar cells have attracted a lot of interest. High performance GaP solar cells require good surface passivation. Thus here we use AlGaP for the first time as a surface passivation layer for these solar cells. To study this passivation effect, we have designed a novel growth procedure. Initial results of our GaP solar cell with an AlGaP front surface passivation layer are promising. We have achieved the highest reported efficiency of 2.90%.

To further improve the surface passivation characteristics, we will need to optimize growth conditions of the AlGaP epitaxial layer. We will need an ultra thin (less than 50 nm) high quality AlGaP front surface passivation layer in order to achieve GaP solar cells with higher performance. Moreover, we will need to optimize the front contact design and metallization procedure in order to achieve higher FF.

REFERENCES

[1] X. Lu, S. Huang, M. Diaz, R. Opila, and A. Barnett, "Design, fabrication, characterization and analysis of wide band gap Gallium phosphide solar cells," in *Proc. 25th Eur. Photovoltaic Solar Energy Conf. Exhibition*, Valencia, Spain, 2010, pp. 212–217.

[2] A. Barnett, D. Kirkpatrick, C. Honsberg, D. Moore, M. Wanlass, K Emery, R. Schwartz, D. Carlson, S. Bowden, D. Aiken, A. Gray, S. Kurtz, L. Kazmerski, M. Steiner, J. Gray, T. Davenport, R. Buelow, L. Takacs, N. Shatz, J. Bortz, O. Jani, K. Goossen, F. Kiamilev, A. Doolittle, I. Ferguson, B. Unger, G. Schmidt, E. Christensen, and D. Salzman, "Very high efficiency solar cell modules," *Prog. Photovoltaics Res. Appl.*, vol. 17, no. 1, pp. 75–83, 2009.

[3] A. Cornfeld, P. Patel, J. Spann, D. Aiken, and J. McCarty, "Evolution of a 2.05 eV AlGaInP top sub-cell for 5 and 6J-IMM applications," in *Proc. 38th IEEE Photovoltaic Specialists Conf.*, Austin, TX, USA, 2012, pp. 002788–002791.

[4] J. L. Gray, A. Hass, J. Wilcox, and R. Schwartz, "Efficiency of multijunction photovoltaics systems," in *Proc. 33rd IEEE Photovoltaic Specialists Conf.*, San Diego, CA, USA, 2008, pp. 1–6.

[5] S. Jones, J. Ermer, C. Fetzer, and R. King, "Evolution of multijunction solar cell technology for concentrating photovoltaics," *Jpn. J. Appl. Phys.*, vol. 51, no. 10, p. 10ND01, 2012.

[6] C. Allen, J. Woodall, and J. Jeon, "Results of a gallium phosphide photovoltaic junction with an AR coating under concentration of natural sunlight," *Solar Energy Mater. Solar Cells*, vol. 95, no. 9, pp. 2655–2658, 2012.

[7] X. Lu, M. Diza, N. Kotulak, R. Opila, and A. Barnettet, "Quantum efficiency model driven design for wide band gap GaP solar cells," in *Proc. 37th IEEE Photovoltaic Specialists Conf.*, Seattle, WA, USA, Jun. 2011, pp. 000507–000512.

[8] X. Lu, S. Huang, M. Diza, N. Kotulak, R. Hao, R. Opila, and A. Barnett, "Wide band gap Gallium phosphide solar cells." *IEEE J. Photovoltaics*, vol. 2, no. 2, pp. 214–221, 2012.

[9] V. M. Andreev, A. Kazantsev, V. Khvostikov, E. Paleeva, V. Rumyantsev, and M. Shvarts, "High-efficiency (24.6% AM 0) LPE grown AlGaAs/GaAs concentrator solar cells and modules," in *Proc. 24th IEEE Photovoltaic Specialists Conf.*, Waikoloa, HI, USA, Jun. 1994, pp. 2096–2099.

[10] Z. S. Bittner, D. V. Forbes, M. Nesnidal, and S.M. Hubbard, "GaP solar cells with InGaP quantum wells for high temperature application," in *Proc. 37th IEEE Photovoltaic Specialists Conf.*, Seattle, WA, USA, 2011, pp. 001959–001964.

[11] K. H. Montgomer, C. R. Allen, I. H. Wildeson, J. H. Jeon, A. K. Ramdas, and J. M. Woodall, "Gettered GaP substrates for improved multijunction solar cell devices," *J. Electron. Mater.*, vol. 40, no. 6, pp. 1457–1460, 2012.

[12] J. Zhao, A. Wang, M. Green, and F. Ferrazza, "Novel 19.8% efficient "honeycomb" textured multicrystalline and 24.4% monocrystalline silicon solar cells," *Appl. Phys. Lett.*, vol. 73, no. 14, pp. 1991–1993, 1998.

[13] T. Prutskij, V. Andreev, and V. Larionov, "GaP-AlGaP heterojunction photosensors with photosensitivity maximum at 380–420 nm," *Solar Energy Mater. Solar Cells*, vol. 37, nos. 3–4, pp. 349–355, 1995.

[14] X. Mei, H. Ruda, T. Berdiskihk, and M. Buchana, "Liquid phase epitaxial growth of GaP layers on textured GaP(111)B substrate," *J. Cryst. Growth*, vol. 193, nos. 1–2, pp. 148–155, 1998.

[15] J. T. Longo, J. S. Harris, E. R. Gertner, and J. C. Chu, "Improved surface quality of solution grown GaAs and Pb$_{1-x}$Sn$_x$Te epitaxial layers: A new technique," *J. Cryst. Growth*, vol. 15, no. 2, pp. 107–116, 1972.

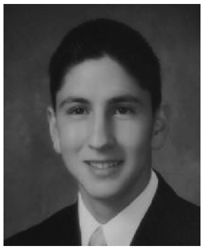
[16] T. Sugiura, A. Tanaka, H. Unno, and T. Sukegawa, "LPE growth of uniform (Ga,Al)P alloy crystal," *Jpn. J. Phys.*, vol. 22, no. 3, pp. 541–545, 1983.

[17] P. Gay, P. Hirsch, and A. Kelly, "The estimation of dislocation densities in metals from x-ray data," *Acta-Metall.*, vol. 1, no. 3, pp. 315–319, 1953.

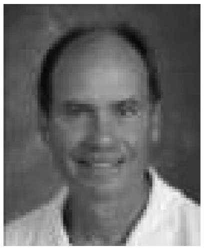
[18] X. Wang, N. Waite, P. Murica, K. Emery, M. Steiner, F. Kiamilev, K. Goossen, C. Honsberg, and A. Barnett , "Lateral spectrum splitting concentrator photovoltaics: Direct Measurement of component and submodule efficiency," *Prog. Photovoltaics Res. Appl.*, vol. 20, no. 2, pp. 149–165, Mar. 2012.

Xuesong Lu (M'09) was born in Fuyang, China. He received the B.S. and M.S. degrees in materials science from Sichuan University, China, in 2003 and 2006, respectively. He received the Ph.D. degree in electrical and computer engineering at the University of Delaware, in 2011. During the Ph.D. study, he mainly focused on the research of high band gap Gallium Phosphide solar cells grown via liquid phase epitaxy method. After his graduation, he joined Applied Materials as a Senior Process Engineer. Currently, he is working on the project of high efficiency crystalline Si solar cells in Applied Materials.

Ruiying Hao started her research in photovoltaics in 2003. In 2006, she received the M.S. degree in materials science and engineering from Sichuan University in China where she worked on CdTe solar cells. In 2011, she received the Ph.D. degree in electrical and computer engineering from the University of Delaware for research on single crystalline thin Si solar cells based on epitaxial absorber. She is currently with Crystal Solar, Inc. on Si solar cells.



Martin B. Diaz was born in Midland, TX. He received the B.S.E.E. degree from the University of Nebraska-Lincoln, in 2009. He received the Ph.D. degree in electrical engineering from the University of Delaware, in 2011. His research interest is in high performance, next generation photovoltaic solar cells. In 2009, he joined the Solar Power Program of the University of Delaware. His present work concentrates on LPE growth of III–V solar cells on silicon.



Robert Opila received the Ph.D. degree in chemistry from the University of Chicago in 1982 and immediately began work at Bell Laboratories. While there, he studied the role of surfaces and interfaces in electronic materials and devices. He was named a Distinguished member of Technical Staff and promoted to Technical Supervisor. In 2002, Opila joined the Department of Materials Science and Engineering at the University of Delaware, where his interest in the surfaces and interfaces of electronic materials has grown to include photovoltaics and thermoelectrics. He is a fellow of the AVS and is currently an editor of *Applied Surface Science*.

Allen Barnett (M'72) joined the School of Photovoltaics and Renewable Energy Engineering, The University of New South Wales, as a Professor of Advanced Photovoltaics in September, 2010. He joined the University of Delaware (UD) in 1976 as Director of the Institute of Energy Conversion and Professor of Electrical Engineering. He left UD in 1993 to devote full time to AstroPower, Inc., which became the largest independent solar cell manufacturer and the fourth largest in the World. He returned to UD in 2003 and was Executive Director, Solar Power Program; Research Professor, Department of Electrical and Computer Engineering; and Senior Policy fellow, Center for Energy and Environmental Policy. Barnett has supervised 26 Ph.D. theses including 7 Ph.D. and 3 M.S. degrees in 2011. Barnett received the M.S. and B.S. degrees in electrical engineering from the University of Illinois, and the Ph.D. degree in electrical engineering from Carnegie-Mellon University. He is a fellow of the *Institute of Electrical and Electronic Engineers* (IEEE). He received the IEEE William R. Cherry Award for outstanding contributions to the advancement of photovoltaic science and technology and the Karl W. Böer Solar Energy Medal of Merit. He has more than 280 publications, 28 U.S. patents, and 7 Research and Development 100 Awards for new industrial products. He actively consults for government agencies, institutional investors, and private companies.