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List of Acronyms

AM1.0	Air Mass 1.0
FWHM	Full Width Half Maximum
GW	Gigawatt
HOVPE	Hydride Organometallic Vapor Phase Epitaxy
HVPE	Hydride Vapor Phase Epitaxy
ITP	Industrial Technology Program
KWh	Kilowatt hour
LED	Light Emitting Diode
MBE	Molecular Beam Epitaxy
MOCVD	Metal Organic Chemical Vapor Deposition
ORNL	Oak Ridge National Laboratory
PL	Photoluminescence
SMI	Structured Materials Industries, Inc.
sccm	standard cubic centimeter per minute
TBTU	tera - British Thermal Unit
TCE	Total Carbon Equivalent
TMIn	Trimethyl Indium
TEGa	Tetraethyl Gallium
UV	Ultraviolet
XPS	X-ray Photoelectron Spectroscopy

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1.0 Executive Summary

The goal of this project was to develop a low-cost and low-energy technology for production of photovoltaic devices based on InGaN and AlGaIn materials. This project builds on two recent and significant technology developments to accomplish this goal. The first is the discovery by Cornell University and Lawrence Berkeley National Laboratory that InGaN and InAlN can be produced with bandgaps across the entire solar spectrum. This discovery opened the door to fabrication of high-efficiency, multi-junction solar cells, entirely from within the GaN-InN-AlN material system. The second technology is the ongoing development by Structured Materials Industries (SMI), of novel thin film deposition technology, which we have named hydride organometallic vapor phase epitaxy (HOVPE) for Group III-Nitride materials. SMI's HOVPE deposition technology has the potential to deposit Group-III nitride materials for solar cells and other devices, at significantly lower costs and significantly lower energy usage compared to conventional deposition techniques, such as molecular beam epitaxy (MBE) or metal organic chemical vapor deposition (MOCVD).

The critical feature of SMI's deposition technology is to use metallic sources for some portion of the Group-III elements (i.e. Ga, In and/or Al), instead of solely metalorganic sources as is traditionally used. This can result in a significant cost reduction, since the metallic forms of In, Ga and Al are much cheaper than their corresponding metalorganic compounds, on a molar basis. The use of metallic sources can also result in much faster deposition rates, meaning more solar cells are produced for the same amount of time at high temperature. This reduced thermal requirement means much less energy is needed to produce a given increment of solar cell area.

During this Industrial Technology Program (ITP) Grand Challenge project, SMI demonstrated deposition of GaN and InGaIn films using metalorganic sources, along with the critical transport catalyst needed to use metallic sources. We demonstrated compatibility of the process with standard substrate materials and hardware components. We demonstrated GaN film growth rates up to nearly 10 microns per hour, using metalorganic sources, and InGaIn films with up to 5 molar percent In. For deposition of GaN and InGaIn films using metallic sources, considerable difficulty was encountered. Several technical issues needed to be identified and resolved during this Stage 2 project. Due to these challenges, a limited range of nitride films were produced using metallic sources during the course of this project. However, SMI was able to demonstrate both GaN and InGaIn film deposition from metallic sources, using SMI's HOVPE process, in subsequent work outside of the time frame of this ITP Grand Challenge project.

SMI is presently continuing to develop HOVPE technology for Group-III Nitride films for a variety of applications. The successful development of low-cost, low-energy deposition technology for Group-III Nitride films will result in lower cost solar cells, as well as many other products such as high power devices, high frequency devices, and light emitting diodes (LED's) for display and solid state lighting applications.

Other accomplishments for SMI, which can be attributed in part to this effort include:

- SMI has achieved more than \$ 1.15 million in commercial sales of III-Nitride film deposition tools, due in part to the efforts of this project.
- SMI, Oak Ridge National Laboratory and the University of California at Santa Cruz have received a 2011 R&D 100 Award, due in part to the efforts of this project.

2.0 Introduction

Solar power offers the potential to provide a significant portion of our energy needs, without consumption of fossil fuels or emission of green house gases. However, the manufacture of solar cells can be a costly process, both in terms of dollars and energy consumed. In order for solar power to have a significant positive impact on energy needs and the environment, solar cell manufacturing processes must be low cost and low energy consumption. A convenient way to illustrate this point is to calculate the payback time for solar cells to repay the energy needed to produce them. These calculations and their results are presented in Section 5.0 of this report. In order to be practical, this energy payback time must be much shorter than the expected useful lifetime of the solar cell.

Materials from the group-III nitride family (such as GaN and InGaN) can be used to make high efficiency solar cells, as well as many other products. Thus far, the main limitation to InGaN device implementation has been the high cost and high energy requirements of production technologies such as molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). These techniques are too slow and too expensive for commercial production of all but the most high-end of products. Structured Materials Industries, Inc. (SMI), is presently developing a novel deposition technique for InGaN and related Group III-Nitride materials, which we call hydride organo-metallic vapor phase epitaxy (HOVPE). This process combines the high deposition rates and low equipment costs of hydride vapor phase epitaxy (HVPE) with the excellent process control and material quality of MOCVD. The HOVPE process reduces energy usage, by reducing the time required for the high-temperature, high-vacuum process to deposit device layers, potentially by as much as a factor of 100. The HOVPE process also reduces manufacturing cost by using metallic sources instead of metalorganics. Solar cell production using the InN-GaN-AlN material system will also save energy and cost by reducing the number of manufacturing steps for multi-junction solar cell manufacturing.

The successful implementation of SMI's HOVPE technology, along with recent developments in InGaN and AlGaN materials technology from Cornell University and Lawrence Berkeley National Laboratory, can lead to multi-junction solar cells with efficiencies comparable to (or greater than) competing multi-junction solar cells based on GaInP/GaAs/Ge. These InGaN/AlGaN solar cells could be produced using less than 75% of the energy required to fabricate comparable GaInP/GaAs/Ge solar cells, and with overall production cost reduced by greater than 50%. The availability of abundant, low cost solar power will have significant impact on the US economy, as well as reduce greenhouse gas emissions and reduce US dependence on imported oil. The low-cost, high-rate deposition technology for group-III Nitride materials could also benefit manufacturing processes for many other products, including control devices for high power applications, high frequency analog devices for radar and communications, blue/UV LED's for displays, memory devices and solid state lighting, and UV LED's for water purification.

3.0 Background

There are two main approaches to utilizing solar cells for meeting energy production needs; large numbers of low cost cells or smaller numbers of high efficiency cells. Low cost, low efficiency solar cells are typically produced as single junction devices, from low cost semiconductor materials such as silicon. Low cost cells are typically used in small scale applications, such as portable electronics and remote (off-grid) power sources. For large scale commercial and electric utility applications, better economy is expected when using high efficiency cells with solar concentrators. High efficiency cells are typically multi-junction devices, based on III-V semiconductors. Figure 1 shows the road map for solar cell development [1]. The present state of the art for high efficiency solar cells is the triple-junction lattice-matched cell, based on a GaInP ($E_g = 1.85$ eV) top cell, a GaAs ($E_g = 1.42$ eV) middle cell and a Ge ($E_g = 0.66$ eV) bottom cell in an active Ge substrate, as shown in Figure 2. The multi-junction design is intended to capture a large portion of the energy distribution from the solar spectrum, by stacking several cells with different bandgaps in tandem. Although efficiencies for triple junction cells have been steadily improving due to improved manufacturing, this technology is maturing. Conversion efficiencies are presently around 30% for triple junction cells, and are not expected to significantly exceed these levels without resorting to five or six junction designs [2]. Further improvement is restricted by the material constraints of maintaining lattice matching to readily available substrates such as GaAs or germanium, as illustrated in Figure 3.

Figure 1: Projected road map for solar cell development. From Reference [1].

With options for lattice matched photovoltaics nearly exhausted, present development is focused on lattice mismatched materials [3]. A typical structure for a lattice-mismatched multi-junction solar cell includes a GaInAs cell, with approximately 8% In, to achieve a band gap of $E_g = 1.0$ eV. The GaInAs layer has a significant lattice mismatch ($\sim 2\%$) to commonly used substrate materials such as Ge or GaAs, and to presently mature upper cell materials such as GaAs and

GaInP. The major challenge in developing multi-junction cells with lattice mismatched materials is controlling lattice defects at the mismatched interface, which can propagate through upper layers and effect subsequently grown cells. While lattice mismatched cells may provide the next incremental improvement in conversion efficiency, the increased manufacturing complexity adds considerably to their already high cost. Clearly, new concepts are needed to develop solar cells which are both efficient and economical.

Figure 2: Typical structure for present generation triple junction, lattice matched solar cells.

Figure 3: Lattice matching constraints for present generation triple-junction solar cells.

In 2002, it was discovered by Cornell University and Lawrence Berkeley National Laboratory that InGaN and InAlN can be produced with bandgaps across the entire solar spectrum [4], as shown in Figure 4. This was a very significant discovery, which opened the door to fabricate high efficiency, multi-junction solar cells, all from within the GaN-InN-AlN material system. The bandgaps of the individual cells can be tailored to extract maximum energy from the solar spectrum, with minimal restraints on matching lattice constants. It is predicted that this single family of materials will result in the highest efficiency solar cells (above 50% efficiency) and have significant manufacturing cost advantages. Cornell University is also the first (and so far the only) lab to create one of the critical components for InGaN solar cells, namely *p*-type InGaN throughout the entire composition range. In addition, InAlN has been produced in the range of compositions for solar cell application and *p*-type conductivity has been demonstrated.

Thus far, the Cornell University work has been done using molecular beam epitaxy (MBE) to deposit the InGaN and InAlN materials. While MBE provides an excellent research approach for materials and device development, the technique is far too slow and too expensive for economical solar cell production. An alternative production technology would be metal organic chemical vapor deposition (MOCVD), which also provides excellent film composition and thickness control. However, MOCVD can also be expensive for Group-III Nitride materials,

due mainly to high costs for the metal organic precursors and low deposition rates, particularly when thick (greater than a few μm) layers are required.

Figure 4: Recently determined bandgap energy for the GaN-InN and AlN-InN systems, compared to the AM1.5 solar spectrum.

Structured Materials Industries is developing a novel production technique for InGaN and related Group III-Nitride materials, which we call hydride organo-metallic vapor phase epitaxy (HOVPE). This process combines the high deposition rate and low equipment costs of hydride vapor phase epitaxy (HVPE) with the excellent process control and material quality of MOCVD. HOVPE uses significantly lower cost source materials than MOCVD; namely pure metals instead of metal organics. For example, tri-ethyl gallium (TEGa) is approximately 10 times the cost of metallic gallium. HOVPE also consumes lower amounts of critical gases such as ammonia and hydrogen, as compared to MOCVD. The largest effect on cost is the higher HOVPE growth rate, which can range up to 100 $\mu\text{m/hr}$ for GaN alloys, compared to the typical 1.0 $\mu\text{m/hr}$ for MOCVD. These higher deposition rates along with faster cycle times mean higher wafer throughput for HOVPE, which translates directly to lower capital and labor costs per device. HOVPE may also yield better film purity than MOCVD, particularly regarding carbon contamination.

SMI's HOVPE process has the high deposition rate and high materials purity of conventional HVPE. The main advantage over conventional HVPE is the combination of MOCVD, for better control of doping and fine layer structures. For example, control of Indium incorporation by conventional HVPE is difficult when using indium metal as the source. Using tri-methyl indium (TMIn) as the indium source along with HVPE growth of GaN from gallium metal, results in higher Indium incorporation and better composition control. Conventional HVPE also has difficulty with *p*-type dopants for III-N compounds, such as Mg. Best results for Mg doping are obtained using a metal organic source for the Mg. SMI's HOVPE process represents the best combination of high deposition rate and excellent process control in a single tool. Our HOVPE system also has the significant advantage of being capable of depositing all device layers in a single tool, potentially even in a single process run.

4.0 Results and Discussion

4.1 GaN and InGaN Film Deposition using Metalorganic Sources

Figure 5: The HOVPE *test* reactor at SMI, for low-cost deposition of Group III-Nitride films.

Figure 5 shows the SMI HOVPE *test* reactor, set up for both metallic sources (HVPE mode) and metalorganic sources (MOCVD mode). The system can use either process, or a combination of both in a single process run. A critical aspect of using metallic source materials is the catalyst used for vapor transport of the metal. At the start of this work, little was known about the compatibility of this catalyst with the metalorganic precursors, or with the hardware and component technology used for MOCVD. An initial goal for this program was to establish baseline processes for GaN and InGaN films, with and without the catalyst, and determine the effects of the catalyst on the deposition process and the resulting materials. It should be noted that the test systems metal source offers considerably less evaporation surface area than general HVPE systems and this limits achievable fluxes – this is being rectified in future systems.

The substrates used in this work were 2 inch (0001) sapphire wafers with a 5 μm GaN template layer, supplied by our partners at Veeco as part of their matching contribution to this project. Figures 6A and 6B show examples of the resulting as-deposited wafers, illustrating the uniform, transparent films. Figure 7 shows x-ray diffraction (XRD) results for a GaN film deposited at SMI, onto the Veeco GaN template substrate. The XRD results show only (000 ℓ) type peaks for

GaN, indicating a single crystallographic orientation for the deposited film and the substrate. The fact that the deposited layer is indistinguishable from the substrate indicates excellent epitaxy to the GaN template layer. The growth rate for GaN films followed the expected behavior with precursor flow rate, as shown in Figure 8. The growth rate increase with precursor flow rate, reaching a maximum value of just under 10 microns per hour at around 100 sccm.

Figure 7: X-ray diffraction results for a 4.2 μm thick GaN film deposited at SMI on top of 5.0 μm thick GaN on (0001) sapphire. The results indicate excellent homoepitaxy.

Figure 8: Growth rate versus precursor flow rate for GaN films deposited at SMI for a given set of parameters. Note the test system had limited metal source surface area.

The MOVPE process requires a proprietary catalyst, for growth of III-Nitride films using metallic sources. The catalyst is not needed for film growth using metalorganic sources. However, the overall fabrication process for solar cells using our MOVPE process will require film growth using both metallic and metalorganic sources in the same process chamber. Therefore, it was imperative to determine the effect of the catalyst on the growth process and on the resulting films, when using metalorganic sources.

At the beginning of this project, little was known about the effect of the catalyst on growth of Group III-Nitride films using metalorganic sources. The results of this project add significantly to this knowledge base. The presence of the catalyst had only a marginal effect on the GaN film growth rate using a metalorganic gallium source, as shown in Figure 9. Reasonable growth rates ($> 5.0 \mu\text{m/hr}$) are observed at zero catalyst flow. Adding catalyst appears to decrease the growth rate for GaN slightly at both 200 Torr and 600 Torr total chamber pressure. The presence of the catalyst had no effect on material quality, as measured by the x-ray diffraction peak widths. Figures 10 and 11 show results for x-ray rocking curve analysis for the (102) and (002) GaN diffraction peaks. The data show the x-ray peak widths (full width at half maximum or FWHM). Smaller values indicate a greater degree of crystal quality. Crystal quality was relatively good for the GaN films, with FWHM values around 175 and 300 arcsec for the (102) and (002) peaks respectively. Addition of the catalyst appears to have no effect on crystal quality for deposition at either 200 Torr or 600 Torr.

Figure 9: Growth rate as a function of catalyst flow for GaN films deposited at SMI.

Figure 10: X-ray rocking curves for the GaN (102) peak, for GaN films deposited at SMI using a metalorganic source.

Figure 11: X-ray rocking curves for the GaN (002) peak, for GaN films deposited at SMI using a metalorganic source.

4.2 Identification of InGaN Film Segregation Issues

One of the issues encountered during this program was with compositional segregation during deposition of the InGaN film. The issue was initially identified through electrical characterization of the films at Cornell University. For some InGaN films, the sheet resistivity measured by non-contact Hall measurements showed the films to have a low sheet resistivity and a relatively high Hg probe contact resistance. Figure 12 shows the Ohmic resistance between Hg probe contacts with Non-Contact Hall sheet resistivity, compared with InN films produced by MBE at Cornell. The results indicate there is a surface layer with different electrical properties than the interior of the films.

In depth analytical work was done at Oak Ridge National Laboratory to diagnose the issues with InGaN films. Selected samples were analyzed by x-ray photoelectron spectroscopy (XPS). Argon sputter depth profiles were done using XPS to measure the composition. Figure 13 shows an example XPS scan, used to determine composition of the InGaN films. Figure 14 shows XPS sputter depth profile results

Figure 12: Hg probe contacts resistance versus Non-Contact Hall sheet resistivity for InGaN films deposited at SMI, compared with InN films produced by MBE at Cornell.

Figure 13: Representative x-ray photoelectron (XPS) scan, used to determine composition for InGaN films deposited at SMI.

for an InGaN film deposited at 740 C. The depth scale of Figure 14 was estimated using the known sputtering rate for SiO₂, and is only approximate for InGaN. The results still serve very well to illustrate the behavior observed for our InGaN films. For this sample, the results show an approximately 20 nm thick layer of InGaN, with approximately 0.5% Indium, deposited on the GaN template layer. Above this In_{0.005}Ga_{0.995}N layer, is an approximately 20 nm thick layer of pure GaN with no Indium.

Figure 14: XPS sputter depth profile results for an InGaN film deposited at SMI with a growth temperature of 740 C.

Figure 15: XPS sputter depth profile results for an InGaN film deposited at SMI with a growth temperature of 700 C.

Figure 15 shows XPS sputter depth profile results for an InGaN film deposited at SMI under similar conditions, but at a growth temperature of 700 C and about 5 times longer deposition time. The results show an approximately 20 nm thick layer of InGaN, with approximately 5% Indium. Above this $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$ layer, is an approximately 70 nm thick layer of pure GaN with no Indium. Two effects appear to be operative. The results indicate that indium incorporation in our InGaN films increases with decreasing deposition temperature. Also, under non-optimum conditions, Indium incorporation appears to stop partway through the deposition process, resulting in a non-uniform distribution of indium throughout the film thickness.

Figure 16 shows results of photoluminescence (PL) measurements on the InGaN film sample deposited at 740 C. This is the same sample used for the XPS analysis of Figure 14. The center graph shows the emission peak due to the overlapping GaN and InGaN bandgap transitions. The lower graph shows the computer deconvolution to two Gaussian peaks. Peak 0 at 364.8 nm (3.40 eV) is the bandgap peak for pure GaN. Peak 1 at 370.59 nm (3.345 eV) is the InGaN bandgap peak. Using previous results generated by Cornell, the In content is estimated at 1% for this film. The PL results are in general agreement with the XPS results shown in Figure 14.

Figure 16: Photoluminescence results for an InGaN film sample deposited at 740 C.

Figure 17 shows the results of similar PL analysis for an InGaN film deposited at 700 C. This is the same sample used for the XPS analysis of Figure 15. Deconvolution of the bandgap emission again shows two peaks. Peak 0 at 365.05 nm (3.40 eV) is the bandgap peak for pure GaN, due to the GaN template wafer used for the substrate. Peak 1 at 388.84 nm (3.188 eV) is the InGaN bandgap peak. As expected, the PL results show two materials are present, InGaN and GaN. Using data generated by Cornell University, we estimate the Indium content for the

InGaN in this sample at 5 molar %. These results are in general agreement with the XPS data of Figure 15 for this sample. The results confirm that we can control indium content in these films, and achieve indium concentrations of 5 molar %, as specified in one of the Milestones for this project.

Figure 17: Photoluminescence results for an InGaN film sample deposited at 700 C.

4.3 Group-III Nitride Film Deposition using Metal Sources

The HOVPE test stand at SMI was also enabled for deposition of GaN and InGaN films using metal sources. Figure 18 shows a close up of the reactor showerhead, with the metal source injector tube installed. Figure 19 shows one version of the quartz injector tube design, with the heater wires and thermocouples installed prior to installation in the HOVPE system. The injector has separate heater and temperature monitors, to keep the gallium source at controlled temperature during film growth. Gallium laden vapors are chemically transported from the injector to the growing film. This process allows growth of the films using metallic sources instead of metalorganic sources, potentially with significant increase in deposition rate and reduction in source material costs.

During the course of this work, we encountered several difficulties in effective operation of the metal sources. The most significant issue was failure of the metal leads to the injector heater, which was resolved by a material substitution in the leads. Figure 20 shows the metal injector tube loaded with metallic gallium. Figure 21 illustrates some of the failure mechanisms which have been observed. The metal source materials can deposit on the exterior of the injector tube, shorting out the heater and thermocouple wires, and leading to electrical failures.

Figure 18: Close view of the showerhead for the modified HOVPE test stand at SMI, showing the installation and external connections for the metal source injector.

Figure 19: A version of the metal source injector design, with the heater wires and thermocouples installed.

Figure 20: (Left) Close up view of the metal source injector loaded with gallium metal, after operation and removal from the HOVPE test stand at SMI.

Figure 21: (Below) Observed failure for the metal source injector after operation in the HOVPE test stand at SMI. The liquid metal has run out of the quartz tubing, which itself has in part melted.

Although no device ready GaN or InGaN films were produced using metal sources during the course of this project, SMI has been able to demonstrate both GaN and InGaN film deposition from metallic sources, using SMI's MOVPE process, in subsequent work outside of the time frame of this first phase of the ITP Grand Challenge project. This subsequent development was accomplished under DARPA funding. Figures 22 and 23 document the achievement.

Figure 22: 1000 X optical micrograph of an InGaN film deposited on GaN using SMI's MOVPE technique. The source materials were metallic Ga, a metalorganic source for In (TMIn), NH_3 and the catalyst.

Figure 23: Measured growth rate versus catalyst flow for InGaN films deposited on GaN using SMI's MOVPE technique. The source materials were metallic Ga, a metalorganic source for In (TMIn), NH_3 and the catalyst.

4.4 HOVPE Tool Evolution Based on this and subsequent/parallel works

Through the course of this work, we adapted to maximizing the output of this program, both in terms of materials and hardware design evolutions. Figures 24, 25, and 26 depict the tooling (hardware) evolution from this, other and subsequent continuing work. Presently SMI's HOVPE technology is at a transitional stage - originally this program could have funded it through to fruition, however since funds for the program were limited we are now seeking follow-on funding wherever possible.

Figure 24: General comparison of *test* scale (~5.8" wafer carriers) reactor design evolution: (left) original in-house test tool design, (right) present state of the art design.

Figure 25: State of HOVPE pilot tool design at the end of this program.

Figure 26: Present HOVPE pilot tool design evolved from this and subsequent work. Note this design includes provision for a water cooled metalorganic source; shown at bottom right.

5.0 Benefits Assessment

SMI and ORNL have developed models to assess the potential benefits of our low cost production technology for III-Nitride based photovoltaics. The energy, economic, and environmental benefits associated with the technology are presented in two major parts:

1. The benefits from low energy production of photovoltaic devices using SMI's HOVPE technology.
2. The benefits from using these devices in renewable energy production.

Benefits from low energy production of photovoltaic devices using SMI's HOVPE technology:

Table I compares the energy needed to produce various types of solar cells. Silicon based single junction cells presently require about 15.6 watt-hours per square centimeter to fabricate [5]. These same cells will produce about 0.01 Watts under typical AM1.0 solar conditions. Thus a typical silicon photovoltaic needs to operate for about 1,560 hours to repay the energy needed to produce it. In comparison, present technology triple junction photovoltaics require nearly 1100 watt-hours per square centimeter to fabricate. While these cells are much more efficient than conventional silicon photovoltaics, the high fabrication energy precludes their use in most terrestrial applications. High efficiency, multi-junction solar cells are typically used for space based power, where the high launch cost justifies their use on a per kilogram basis.

Table I also shows the anticipated energy needed to fabricate InGaN/InAlN multi-junction solar cells using SMI's HOVPE process. For these calculations, we assumed the multi-junction cells would use a substrate such as germanium or sapphire, and thus substrate and substrate processing energy requirements would be similar to silicon. We also assumed the back-end processing and module fabrication requirements would be similar to silicon photovoltaics. The main difference is assumed to be the process steps to deposit the compound semiconductor layers to form the additional junction devices. For present technology triple-junction photovoltaics, these layers are deposited by MBE or MOCVD. For our proposed InGaN/InAlN photovoltaics, these layers would be deposited at about 100 times the growth rate, using SMI's HOVPE process.

	Silicon Photovoltaics	Present Triple Junction	HOVPE Triple Junction
Energy to Fabricate (Watt-hrs/cm ²)			
Substrate Growth	4.7	4.7	4.7
Substrate Processing	3.1	3.1	3.1
Multi-Layer Film Deposition		1081.2	10.8
Back End Processing	3.1	3.1	3.1
Module Fabrication	4.7	4.7	4.7
Total Energy to Fabricate	15.6	1096.8	26.4
Efficiency	10%	35%	35%
Output (W/cm ²)	0.010	0.035	0.035
Repayment Time (hrs)	1,560	31,336	755

Table I: Energy needed to fabricate various types of solar cells in Watt-hours/cm².

Note that while our proposed InGaN/InAlN cells still requires about twice the energy to fabricate than conventional silicon photovoltaics, this is more than offset by the factor of 3.5 increase in efficiency. This actually represents a conservative estimate, in which we have assumed the anticipated efficiency of our InGaN/InAlN cells to be comparable to present technology triple-junction solar cells. Actually, we anticipate even greater efficiency for our proposed solar cells (up to about 50%), since we have far greater latitude to tailor the bandgap energies and thus better utilize the entire solar spectrum.

Table II shows the required solar cell area, and the calculated production cost to fabricate enough cells to reach 5.0 GW total capacity, which is the anticipated market penetration for these solar cells by the year 2030. Total energy savings of over 4.0 billion kilowatt-hours is expected. In Table III, we estimate the yearly and cumulative energy and cost savings due to fabricating 5.0 GW of solar power capacity using SMI's HOVPE triple junctions cells, compared to the same power capacity of silicon based single junction cells. We also show the yearly and cumulative reductions in pollutants and greenhouse gases that go along with this energy savings. Keep in mind that up to this point we are only talking about the benefits of the low energy processes to fabricate these solar cells. Additional economic and environmental benefits will be realized when these solar cells are put into use.

Table II: Total energy expenditures to produce 5 GW solar capacity for various solar cells.			
	Silicon Photovoltaic	Present Triple Junction	HOVPE Triple Junction
Area required for 5 GW total capacity (cm ²)	5.00 x 10 ¹¹	1.42 x 10 ¹¹	1.42 x 10 ¹¹
Energy expenditure for 5 GW total capacity (KWh)	7.80 x 10 ⁹	1.55 x 10 ¹¹	3.75 x 10 ⁹

Table III: Energy and environmental benefits of fabricating 5 GW of solar cell capacity using SMI's HOVPE triple-junction technology, compared to fabricating 5 GW of present silicon based solar cells.			
Metric	Yearly Impact by 2020	Yearly Impact by 2030	Cumulative Impact by 2030
Primary energy displacement (TBTU)	20.39	66.43	555.7
Energy-cost savings (\$MM)	123.4	412.5	3395
CO ₂ emissions displaced (MM Tonnes TCE)	0.400	1.29	10.81
SO ₂ emissions displaced (Metric Tonnes)	5349	17424	146,210
NO _x Emissions Displaced (Metric Tonnes)	3512	11,440	95,831

Benefits of using the high efficiency solar cells in renewable energy production:

Table IV shows the amount of consumption of the three major non-renewable resources for electricity production, and the estimated savings from installation of 5.0 GW capacity of our proposed high efficiency solar systems. Table V shows the reduction in consumption of non-renewable resource, due to generation 5.0 GW of renewable energy using our proposed high efficiency solar systems.

Table IV: Estimated reduction in consumption of non-renewable resources, due to installation of 5.0 GW capacity of our proposed high efficiency solar systems.

Resource	2007 Consumption	Savings estimated each year by 2030
Coal	1,046,795 x 10 ³ tons	6184 x 10 ³ tons
Petroleum derivatives	112,615 x 10 ³ barrels	663 x 10 ³ barrels
Natural gas	7,089,342 x 10 ⁶ cubic feet	41,841 x 10 ⁶ cubic feet

Table V: Estimated yearly and cumulative energy and cost savings, due to installation of 5.0 GW capacity of our proposed high efficiency solar systems.

Metric	Yearly Impact by 2020	Yearly Impact by 2030	Cumulative Impact by 2030
Primary energy displacement (TBTU)	120.55	392.67	3279.09
Energy-cost savings (\$MM)	287.21	960.79	7949.28

In the preceding discussions, the following assumptions were used to calculate the yearly and accrued benefits associated with installation of the proposed high efficiency solar cell systems:

1. The total installed solar cell capacity by the year 2030 will be 100 GW [6].
2. The first year of commercial production of our proposed HOVPE triple junction technology will be 2015.
3. Annual sales growth rate = 5%.
4. Years to saturation of technology = 5 years.
5. Market share of technology = 5% (= 5.0 GW installed capacity in 2030).
6. Electricity produced through increase in solar generation displaces electricity produced through non-renewable resources such as coal, petroleum and its derivatives and natural gas.
7. Displacement of each of these resources is proportional to their contribution to generation capacity from each of these resources in 2007 [7].

6.0 Commercialization

SMI has achieved \$ 1.15 million in commercial sales of III-Nitride film deposition tools, due in part to the efforts of this project. These sales included 2 tools sold to government research laboratories and one tool upgrade to an industrial customer. In addition, SMI has also achieved significant sales of III-Nitride service work from industrial customers, based in part on the efforts of this project.

7.0 Accomplishments

- Demonstrated technical feasibility of the HOVPE process for producing GaN and InGaN films using metallic sources.
- Demonstrated deposition of GaN films at growth rates over 9 microns per hour, and InGaN films with In concentrations up to 5 molar per cent.
- SMI has achieved more than \$ 1.15 million in commercial sales of III-Nitride film deposition tools, due in part to the efforts of this project.
- SMI, Oak Ridge National Laboratory and the University of California at Santa Cruz have received a 2011 R&D 100 Award, due in part to the efforts of this project.
- Veeco provided matching funds to this program for further evaluation of catalyst enhanced metalorganic film deposition.
- SMI significantly refined production tool designs.

8.0 Conclusions

During this ITP Grand Challenge project, SMI demonstrated deposition of GaN and InGaN films using metalorganic sources, along with the critical transport catalyst needed to use metallic sources. We demonstrated compatibility of the process with standard substrate materials and hardware components. We demonstrated GaN film growth rates up to nearly 10 microns per hour, using metalorganic sources. However, the observed growth rate for InGaN was much lower. For deposition of GaN and InGaN films using metal sources, considerable difficulty was encountered. Several technical issues were identified and resolved; including that the catalyst cannot be introduced in our system under present conditions with the metalorganics but should be done separately. Due to these challenges, no device GaN or InGaN films were produced using metal sources during the course of this project. However, SMI was able to demonstrate both GaN and InGaN film deposition from metallic sources, using SMI's HOVPE process, in subsequent work outside of the time frame of this ITP Grand Challenge project.

SMI is presently continuing to develop HOVPE technology for group-III Nitride films for a variety of applications. The successful development of low-cost, low-energy deposition technology for group-III Nitride films will result in lower cost solar cells, as well as many other products such as high power devices, high frequency devices, and light emitting diodes (LED's) for display and solid state lighting applications.

9.0 Recommendations

While the HOVPE technique has been shown to be technically feasible, much more development work is needed in order to bring this technology to a commercial manufacturing level. This work is presently continuing at SMI and SMI's customers. SMI has gained many proprietary insights into how to improve the HOVPE process. These process and hardware solutions are presently being implemented.

Further development work is also recommended, to apply the HOVPE process to many other products based on group-III Nitride materials, including high power devices, high frequency devices, and light emitting diodes.

10. References

1. D.C. Senft, "Applications for GaInN in Solar Cells", AFOSR Indium Nitride Workshop 2, 9-13 January (2005).
2. F. Dimroth, "High-efficiency solar cells from III-V compound semiconductors", *Phys. Stat. Sol.*, Vol. 3(3), p. 373 (2006).
3. M.W. Wanlass, S.P. Ahrenkiel, R.K. Ahrenkiel, D.S. Albin, J.J. Carapella, A. Duda, J.F. Geisz, Sarah Kurtz, T. Moriarty, R.J. Wehrer and B. Wernsman, "Lattice-Mismatched Approaches for High-Performance, III-V Photovoltaic Energy Converters", 31st IEEE Photovoltaics Specialist Conference, Orlando, FL, Jan 3-7 (2005).
4. J. Wu, W. Walukiewicz, K.M. Yu, J.W. Ager, E.E. Haller, H. Lu, W.J. Schaff, Y. Saito and Y. Nanishi, "Unusual properties of the fundamental band gap of InN", *Applied Physics Letters*, Vol. 80(21), id. 3967 (2002).
5. "Silicon Info: Single-Crystal Ingot Growth", May (2007), available at <http://www.siliconsultant.com/SIcrysgr.htm>.
6. "Multi-year Program Plan, Solar Energy Technologies Program 2008-2012", U.S. Department of Energy, EERE, April 15, (2008).
7. "Existing Capacity by Energy Source 2007," *Electric Power Annual* with data for 2007, January 21, 2009, Energy Information Administration, Official Energy Statistics from the US Government (2007).