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High Efficiency InP Solar Cells from Low Toxicity Tertiarybutylphosphine

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Large scale manufacture of phosphide based semiconductor devices by organo-metallic vapor phase epitaxy (OMVPE) typically requires the use of highly toxic phosphine. Advancements in phosphine substitutes have identified tertiarybutylphosphine (TBP) as an excellent precursor for OMVPE of InP. High quality undoped and doped InP films were grown using TBP and trimethylindium. Impurity doped InP films were achieved utilizing diethylzinc and silane for p and n type respectively. 16 % efficient solar cells under air mass zero, one sun intensity were demonstrated with V_{oc} of 871 mV and fill factor of 82.6%. It was shown that TBP could replace phosphine, without adversely affecting device quality, in OMVPE deposition of InP thus significantly reducing toxic gas exposure risk.

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Indium phosphide (InP) and InP based semiconductor materials are widely used for optoelectronic applications. High efficiency solar cells^(1,2) have been produced which demonstrate excellent radiation resistant properties.⁽²⁻⁴⁾ The most efficient cells are fabricated using organo-metallic vapor phase epitaxy (OMVPE) to deposit n/p junctions on single crystal substrates. The method of depositing InP typically requires the use of phosphine (PH₃) and trimethylindium (TMIn) precursors. While excellent InP films can be deposited using these precursors, as demonstrated by very high mobility undoped layers with carrier concentrations below 1×10^{14} carriers/cm³, the extreme toxicity of PH₃ poses a barrier in large scale commercial production of InP. PH₃ (Threshold Limit Value (TLV) of 0.3 ppm)⁽⁵⁾ is extremely toxic and lethal at very low concentrations (Lethal Concentration for 50% of population (LC₅₀) for rats of 11 ppm). Scale up of InP growth in production facilities would require large amounts of PH₃ since it must be supplied in excess to the OMVPE reaction process. Significant exposure risk would result in a manufacturing environment using PH₃.

Because of these environmental and safety considerations, efforts have been made to develop substitute precursors suitable for the OMVPE process.^(6,7) Tertiarybutylphosphine (TBP) has been identified as a possible low toxicity substitute for PH₃. TBP is not considered to be a poison and has a TLV of 1100 ppm. It is supplied as a liquid with a very suitable vapor pressure for introduction to the OMVPE reactor. Excellent InP films can be grown at lower temperatures and at lower V/III ratios than with PH₃.^(8,9) At present, however, applications have been limited to microwave devices. Large area devices, such as solar cells, that require long minority carrier lifetimes for efficient operation, have not been investigated.

In this article, we report the growth of high quality, high lifetime InP devices using TBP and TMIn. Undoped InP was grown to establish that our reactor was capable of high quality material growth. Doping studies were then carried out to characterize the growth process in preparation for device fabrication. Finally, we show that it is possible to produce InP n+/p solar

cells with output characteristics that compare favorably with the best state-of-the-art PH_3 grown devices.

Growth of InP was performed in an OMVPE reactor of our own design and construction. It is characterized as a horizontal, subatmospheric pressure system. The quartz reaction vessel has an internal liner which is circular in cross section at the inlet and expands gradually into a rectangular cross section. The substrate rests on a silicon carbide coated graphite susceptor heated by a solid state RF generator and induction coil. Growth temperature is measured by a Pt - PtRh thermocouple embedded in the susceptor. A run-vent gas manifold with pneumatic valves and electronic mass flow controllers injects the precursors into the palladium purified hydrogen carrier gas stream. The system pressure, temperature, mass flow rates and switching are all computer controlled. The reactor was typically operated at 150 torr. Growth was performed by flowing 14.5 $\mu\text{mol}/\text{min}$ TMIIn (Sumitomo) with 0.7 torr partial pressure of TBP (American Cyanamid) over the substrate at a susceptor temperature of 590 $^\circ\text{C}$. Growth rates under these conditions were a very reproducible 2.2 $\mu\text{m}/\text{hr}$ resulting in layers uniform to within $\pm 5\%$ over a 2" diameter wafer. Growth efficiency was found to be $2.5 \times 10^3 \mu\text{m}/\text{mol}$. Doping was achieved by injection of DiethylZinc (DEZn) from a liquid source at -10°C (American Cyanamid) and Silane (SiH_4) diluted to 200 ppm in H_2 (Scott Specialty Gases) for p and n type respectively.

The quality of undoped InP layers was assessed by room temperature Hall characteristics and low temperature photoluminescence (PL). Doped InP films 2 to 4 μm thick were characterized by Hall measurements and photochemical C-V profiling.

Hall measurements showed undoped InP layers to have n-type conductivity with 2×10^{15} carriers/ cm^3 and room temperature majority carrier mobility above 4000 $\text{cm}^2/\text{volt}\cdot\text{sec}$. A PL spectrum from an undoped TBP grown InP sample at 1.5 $^\circ\text{K}$ is shown in Fig. 1. The luminescence was excited by the 514 nm line from an Ar^+ laser at a power density of approximately 12.5 mW/cm^2 . The spectrum shows a well defined near band edge exciton structure common to high

quality InP.^(7,9,10) The free exciton is visible as a shoulder on the 1.4180 eV X-D⁰ peak. The full width half maximum of the X-D⁰ peak was 0.7 meV. The ratio of the X-D⁰ peak to the next largest peak was approximately 45. Other peaks (Fig. 1 inset) seen could be identified as a D-A for carbon⁽¹¹⁾ at 1.3755 eV and a possible deep donor or donor vacancy complex⁽¹²⁾ at 1.3900 eV.

Doped InP in the appropriate ranges for the n⁺/p solar cells was achieved. Hall and c-v measurements revealed n type carrier concentration of 3×10^{18} carriers/cm³ at a SiH₄ mole fraction of 4.7×10^{-7} . A DEZn mole fraction of 1.4×10^{-7} gave p type conductivity at 1×10^{17} carriers/cm³.

Incorporation of dopants into the InP in our study appears more efficient than others⁽¹⁵⁻¹⁷⁾. A calculated distribution coefficient, K_{Si} based on the equation below where X^s and X^v are the composition of Si in the solid and vapor phases respectively, for Si incorporation in our system at 590°C was 2.7×10^{-2} .

$$K_{Si} = \frac{X_{Si}^s}{X_{Si}^v} \quad \text{where} \quad X_{Si}^v = \frac{[SiH_4]}{[TMIn]}$$

This value is slightly higher than for atmospheric grown InP from PH₃ at the same growth temperature.⁽¹⁵⁾ Distribution coefficient for Zn was calculated as 3.1×10^{-3} which agrees well with the data from literature at atmospheric pressure. Other⁽¹⁸⁾ low pressure data show K_{Zn} values for PH₃ grown InP of 2.8×10^{-4} at a growth rate of 2 μm/hr. However, in a second reactor, identical to the one employing TBP, we have grown InP from PH₃ at low pressure and have calculated K_{Si} to be similar to the TBP data. Another explanation for discrepancies could be due to the TMIn bubbler. The solid TMIn in the Sumitomo bubbler is supported on small diameter beads to keep the TMIn transport constant as the source is consumed. This style of bubbler was used

on both of our reactors. Perhaps the actual amount of TMIn carried to the substrate was not accurately known.

Solar cells were fabricated using planar back Au-Zn contact⁽¹³⁾ and a Au-Ge-Au⁽¹⁴⁾ front emitter grid by standard photolithography lift-off techniques. The structure consisted of a 3.5 μm thick p base doped to 1×10^{17} carriers/cm³ grown on a p type substrate doped to $3\text{-}5 \times 10^{18}$ carriers/cm³ without a p⁺ buffer layer. A 50 nm thick n⁺ emitter doped to 3×10^{18} carriers/cm³ was then grown and thinned by chemical etching to 25 to 30 nm after metallization. The anti-reflective (AR) coating was a single layer evaporated silicon monoxide. The resulting 6 mm x 8 mm cells were tested under air mass zero (AM0) spectrum at one sun intensity.

As shown in Fig. 2, conversion efficiencies greater than 16% have been achieved. The open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF) and dark saturation current density (J_0) of this device are compared in Table I with the best state-of-the-art values that have been achieved using a PH₃ source⁽¹⁾. As can be seen, the values of V_{OC} , FF, and J_0 are all comparable with the state-of-the-art values. The only shortfall is in J_{SC} .

Fig. 3 compares the internal quantum efficiencies of the TBP cell and the PH₃ cell. While there are small differences in the short wavelength response, the major discrepancy occurs at long wavelengths, indicating that carriers generated near the rear p-p⁺ interface in the TBP cell thus incorporates any defects that were present at the substrate surface prior to epitaxial deposition.

Another current loss factor (see table) is the lack of a dual layer antireflection coating on the TBP cells. The lower value of J_{SC} in the TBP grown cells can thus be explained as the result of carrier losses at a defective p-p⁺ interface and an inferior anti-reflection coating. Elimination of these defects in the TBP grown cells would reduce and very likely eliminate the TBP-PH₃ J_{SC} differences.

We thus conclude that TBP is a viable alternative precursor for the growth of solar cells and other minority carrier lifetime devices. High quality undoped InP was grown and effective doping of InP grown with TBP was readily achieved. High efficiency solar cells were demonstrated. Exposure risk could be significantly reduced by utilizing TBP in lieu of the traditional PH_3 precursor while maintaining device quality. Simplified effluent treatment and reduced exposure risk are expected to offset the higher cost of the TBP precursor.

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Table 1.

	TBP	PH ₃ *
FF	.826	.824
V _{OC} (V)	.871	.876
J ₀ (A/cm ²)	5.77 x 10 ⁻¹⁷	5.62 x 10 ⁻¹⁷
J _{SC} (A/cm ²)	30.7	36.3
p buffer	No	Yes
Dual layer AR	No	Yes

*Reference 1

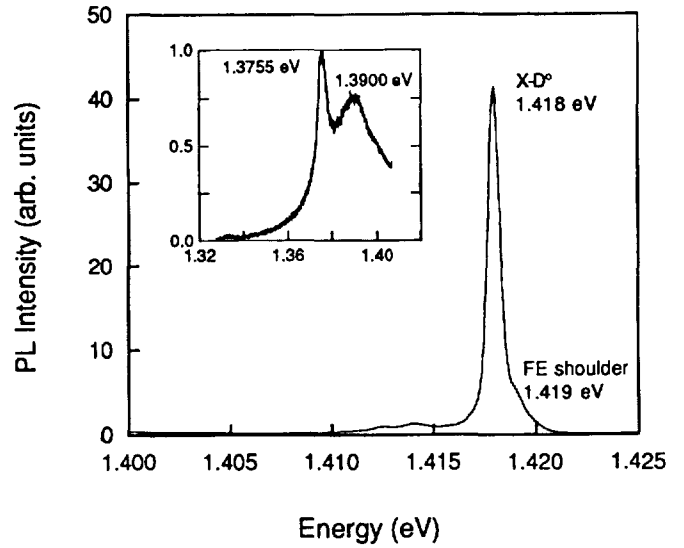


Figure 1.—PL spectrum taken at 1.5 °K from undoped InP grown by OMVPE from TMIn and TBP. Inset is an enlarged view of a portion of the same spectrum.

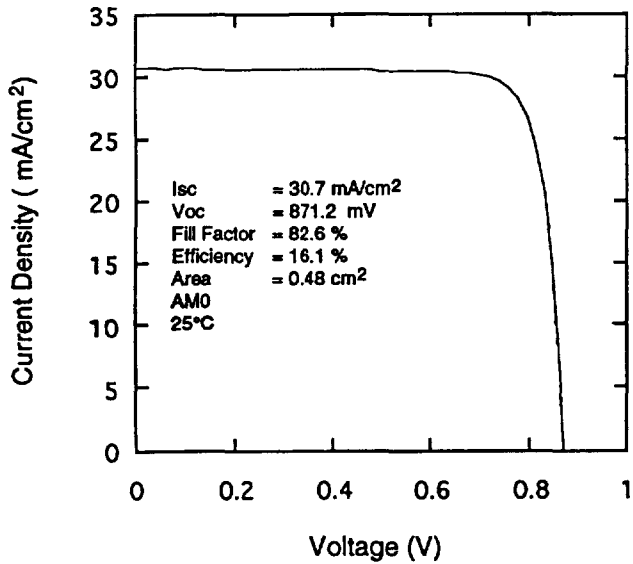


Figure 2.—I-V characteristic of a InP solar cell under 1 sun illumination intensity of the air mass zero spectrum. The n⁺/p cell was produced by OMVPE using TMIn and TBP.

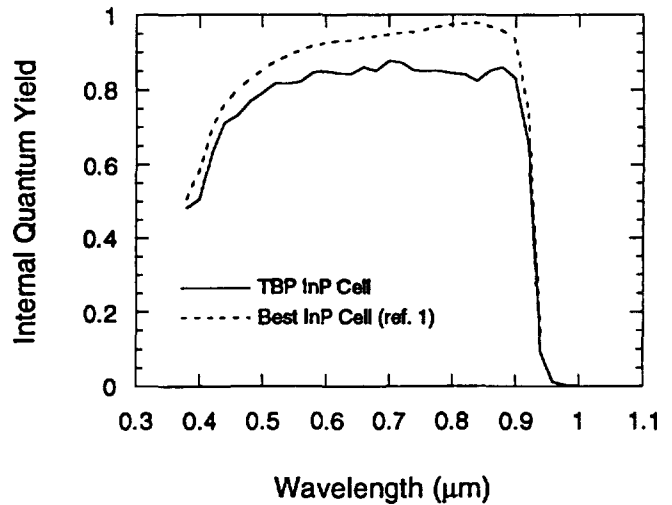


Figure 3.—Internal quantum efficiency from an InP solar cell (without anti-reflection coating) fabricated by OMVPE from TMIn and TBP is compared to the best PH₃ produced InP cell.

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