InAsP/InGaAs Materials Development for 2.1 µm Avalanche Photodiodes

Phase II SBIR contract #N00014-93-C-0254

Dr. Gregory H. Olsen (Principal Investigator)
Dr. Alvin Goodman (Technical Monitor)

QUARTERLY REPORT #5
(9/94 - 12/94)

February 1, 1995

Start Date: Sept. 20, 1993
End Date: Sept. 20, 1995

Sensors Unlimited, Inc.
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Princeton, NJ 08540
(609) 520-0610
(609) 520-0638 (FAX)

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Phase II Statement of Work

The overall technical objective of this program is to advance the state-of-the-art of InAsP/InGaAs materials development so that 2.1 μm APDs which presently do not exist and offer ten times the light detection sensitivity of anything now available can be made.

Specific technical objectives include:

- Development of the hydride vapor phase epitaxial (VPE) compositional grading technique to achieve a lattice mismatch (Δa/a) between the adjacent InAsyP1-y and InxGa1-xAs epitaxial layers of about 0.13% or less.

- Development of innovative annealing techniques to reduce or eliminate lattice mismatch dislocations and thereby reduce the leakage currents of 2.1 μm Avalanche Photodiodes (APDs).

- Fabrication and testing of mesa type APDs for reliability. This will include development of polyimide passivation techniques as well as silicon nitride and silicon oxynitride using Plasma Enhanced Chemical Vapor Deposition (PECVD).

- Calibration of avalanche gain (M) vs. reverse bias (V) at temperatures of 250, 260, 270, 280, 290, and 300K.

- Deliver five APDs having the following characteristics:

<table>
<thead>
<tr>
<th>Active diameter</th>
<th>100 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature spectral response</td>
<td>1.5 - 2.2 μm</td>
</tr>
<tr>
<td>Responsivity at unity gain condition</td>
<td>1.1 A/W @ 2.1 μm</td>
</tr>
<tr>
<td>Avalanche gain @ 0.98 of Vb</td>
<td>10</td>
</tr>
<tr>
<td>Shot noise current</td>
<td>&lt;0.2 nA (rms) in a bandwidth of 100 MHz</td>
</tr>
<tr>
<td>Rise time/fall time</td>
<td>&lt; 5 nsec</td>
</tr>
<tr>
<td>Mean time to failure (MTTF)</td>
<td>1 x 10⁹ hours at 300K</td>
</tr>
</tbody>
</table>
# Phase II Work Schedule

<table>
<thead>
<tr>
<th>Task</th>
<th>Personnel</th>
<th>Months</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Preliminary Design Work</strong>&lt;br&gt;- Overall mask design for 50,100, 200, and 500 ( \mu \text{m} ) diameter devices</td>
<td>GO, MC</td>
<td>0 - 3</td>
</tr>
<tr>
<td><strong>2. Materials</strong>&lt;br&gt;- Calibrate VPE reactor&lt;br&gt;- Etch pit studies for dislocations in InP substrates&lt;br&gt;- Optimize graded layers of VPE In(As,P)</td>
<td>GO, RM</td>
<td>1 - 9</td>
</tr>
<tr>
<td><strong>3. Study Avalanche Breakdown in InAs_{1-4}P_{6}</strong>&lt;br&gt;- Grow VPE InAsP on InP with variable EPD&lt;br&gt;- Fabricate mesa APDs of various diameter&lt;br&gt;- Measure Id, Vg, M vs. diameter and EPD</td>
<td>RM, SF, GO</td>
<td>3 - 9</td>
</tr>
<tr>
<td><strong>4. Fabricate APDs in InAsP</strong>&lt;br&gt;- Optimize thickness/doping profile&lt;br&gt;- Determine optimum geometries</td>
<td>E1, T1, RM</td>
<td>9 - 12</td>
</tr>
<tr>
<td><strong>5. Fabricate InGaAs/InAsP &quot;SAM&quot; APDs</strong>&lt;br&gt;- Confirm thickness/doping profiles</td>
<td>GO, RM, T1</td>
<td>12 - 20</td>
</tr>
<tr>
<td><strong>6. Device Characterization (SAM-APDs)</strong>&lt;br&gt;- Measure Id, Vg, C and M vs diameter&lt;br&gt;- Profile gain across diodes&lt;br&gt;- Measure pulse rise/fall time vs diameter&lt;br&gt;- Perform noise measurements&lt;br&gt;- Measure gain/bandwidth product</td>
<td>GO, RM, T1</td>
<td>14 - 24</td>
</tr>
<tr>
<td><strong>7. Temperature Behavior</strong>&lt;br&gt;- Dark current and gain from 250 to 300K&lt;br&gt;- Spectral cutoffs from 250 to 300K&lt;br&gt;- Noise properties from 250 to 300K</td>
<td>MC, E2</td>
<td>17 - 20</td>
</tr>
<tr>
<td><strong>8. Reliability Studies</strong>&lt;br&gt;- Hermetically seal 100 ( \mu \text{m} ) devices&lt;br&gt;- Bias for 98% of voltage breakdown at 200°C&lt;br&gt;- Measure 20°C Id, Vg, and M every 1000 hours</td>
<td>MC, GO, RM</td>
<td>19 - 24</td>
</tr>
<tr>
<td><strong>9. Deliverables</strong>&lt;br&gt;- Quarterly Reports&lt;br&gt;- 5 APDs&lt;br&gt;- Final Report</td>
<td>GO, RM, SF</td>
<td>24</td>
</tr>
<tr>
<td><strong>10. Phase III Effort</strong></td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>
Figure 1. APD mesa structure which would absorb light out to 2.2 μm. Light absorption takes place in the In$_{73}$Ga$_{27}$As while avalanche multiplication takes place in the uppermost InAs$_{4}$P$_{6}$ layer.
Summary

Early in the quarter we repeated our fabrication of high-bandgap APDs made in abruptly-deposited (no compositional grading) InAsyP1-y grown on P+ InP substrates. A sketch of the structure is shown in Figure 2. This structure, and the measurements performed, is similar to that reported during our Phase I work except that it was grown by organometallic vapor phase epitaxy. In addition, half of each wafer was set aside so that the low bandgap lattice-matched InxGa1-xAs light absorbing layer could be deposited on it if avalanche gain could be produced in the high-bandgap layer alone. Successful results were indeed observed once again. Avalanche gains of 40-80 were typically observed with primary dark currents below 1 nA at 90% of breakdown voltage. These results are reported fully in our revised manuscript for publication, a complete copy of which is attached herein.

Just a few weeks ago, we managed to finish these experiments by depositing the lattice-matched InxGa1-xAs layer onto the unprocessed half of the high-bandgap InAsyP1-y wafer and processed it into mesa detectors. The structure is shown in Figure 3. Nanoamp level dark currents were again observed and measured gains (with a 1.55μm laser) ranged from over 100 (for the 1.87μm cutoff wafer), to 4 for the 2.1μm cutoff wafer. Our initial results are summarized in Figures 4-6 which contain plots of avalanche gain vs reverse bias. Wafer W82 contained InGaAs which would absorb light out to 1.87μm. Gains beyond 100 were measured. Some of the higher results are suspect and will be checked more thoroughly next month. Wafer W83 (2.04μm cutoff) had gains in the 10-20 range which is a more realistic result. The 2.11μm cutoff structure (W84) had gains of
only 3-4. To the best of our knowledge, this represents the first report of avalanche gain in an InGaAs/InAsP structure which could absorb light out to 2.1\textmu m. Detailed measurements will be performed and reported during the next quarter.

**Next Quarter Plans**

We will study the full APD structures in detail, checking for edge breakdown and establishing a calibrated measurement of gain. Spectral measurements will be performed with both white light (out to 2.2\textmu m) and with our 1.98\textmu m laser. Careful noise measurements and structural modifications will then be carried out in future months.

![Diagram](attachment:image.png)

**Figure 2:** Structure used to obtain avalanche gain in high-bandgap InAsP alone.
Figure 3: Similar to Figure 2 with low-bandgap $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited on top to absorb long-wavelength (~2 µm) light.

Figure 4: Avalanche gain vs bias in InAsP/InGaAs APD structure with a 1.84 µm cutoff
Figure 5: Avalanche gain vs bias in InAsP/InGaAs APD structure with a 2.04 μm cutoff
Figure 6: Avalanche gain vs bias in InAsP/InGaAs APD structure with a 2.11 μm cutoff
Avalanche Gain in InAs$_{1-x}$P$_x$ Photodetectors

G. H. Olsen and M. J. Lange
Sensors Unlimited, Inc.
3490 U.S. Route 1 Bld. 12
Princeton, NJ 08540

R. U. Martinelli and N. J. DiGiuseppe
SRI David Sarnoff Research Center
Princeton, NJ 08540

S. R. Forrest
ATC/POEM
Princeton University
Princeton, NJ 08542

Abstract Avalanche gains of 10-40 were observed in undoped InAs$_y$P$_{1-y}$ (0.1< y <0.3) grown directly (without any grading layers) on p-type InP substrates with up to 1% lattice-mismatch. This material has the same lattice parameter as In$_x$Ga$_{1-x}$As (0.6< x <0.7), which absorbs light of wavelength as long as 2.1 μm.
Avalanche photodiodes (APDs) with gains greater than ten for the 1.0 - 1.7 μm spectrum have been available commercially for years using lattice-matched In_{0.53}Ga_{0.47}As/InP epitaxial layers. No such device exists for the region beyond 1.7 μm despite initial attempts using mercury cadmium telluride\(^{(1)}\). Avalanche gain at 2.06 μm would be highly desirable for LIDAR systems, windshear detection and infrared spectroscopy\(^{(2)}\). The present note describes some initial success in the effort to develop such a device.

The proposed structure is shown in Figure 1. It is analogous to the separated absorption and multiplication APD ("SAM-APD") described by Forrest\(^{(3)}\) for In_{0.53}Ga_{0.47}As/InP, whereby light absorption occurs in the "low" bandgap In_{0.53}Ga_{0.47}As/InP while avalanche multiplication takes place in the "high" bandgap InP. The longest wavelength absorbed by the In_{0.53}Ga_{0.47}As is 1.7 μm. To increase this wavelength, additional indium must be added to the In_{x}Ga_{1-x}As (e.g. x=0.70 to absorb 2.2 μm light). This increases its atomic spacing; it is no longer "lattice-matched" to the high-bandgap InP; and misfit dislocations will form between the two materials. Such dislocations act as minority carrier recombination centers, severely degrading device performance. To circumvent this problem, arsenic can be added to the high bandgap InP so that InAs\(_{y}\)P\(_{1-y}\) is used in the high bandgap material. The composition (y) is chosen so that it has the same atomic spacing as the In_{x}Ga_{1-x}As in order to avoid misfit dislocations\(^{(4)}\) that cause microplasmas to form, which reduces the avalanche effect.

The initial question was, can avalanche breakdown be achieved in the InAs\(_{y}\)P\(_{1-y}\)? To examine this question, the simple structure shown in Figure 2 was chosen. Here, InAs\(_{y}\)P\(_{1-y}\) (undoped, n-type) was deposited directly upon a p-type (zinc) InP substrate. Zinc from the substrate would diffuse into the undoped InAsP forming a p/n junction. A mesa structure - formed by bromine/methanol etching\(^{(5)}\) - was used to study the device. This "reverse-bevel" mesa structure has the advantage that the electric field in the interior is always higher than at the mesa edge, thus avoiding edge breakdown\(^{(6)}\).

The epitaxial structure was fabricated with hydride vapor phase epitaxy\(^{(7)}\). This technique has the advantage that it can grow high-quality InP-based alloys at growth rates exceeding 20 μm/hr. Numerous p-i-n (non-avalanche) detectors for the 1.0 - 2.6 μm spectrum have already\(^{(8)}\) been fabricated with this technique. At the growth temperature of 700°C, we estimate that the zinc from the substrate diffuses about 0.5 μm into the 3 μm undoped InAs\(_{y}\)P\(_{1-y}\) layer, which places the p/n junction slightly beyond the misfit dislocations that form at the InAs\(_{y}\)P\(_{1-y}\)/InP interface.
After growth, the wafer was coated with silicon nitride which was subsequently removed everywhere except at the device sites that were in the form of "snowmen", one part being the 100 μm diameter light sensitive region and the other a 50 μm diameter contact region that was subsequently coated with gold. A 1% bromine/methanol solution was used to etch the mesas. Three different wafers were grown and tested, as described in Table 1.

Table 1: 3μm-thick undoped InAsP on a P⁺:InP substrate no grading - direct deposition

<table>
<thead>
<tr>
<th>wafer #</th>
<th>a (Å)</th>
<th>da/a (%)</th>
<th>y</th>
<th>λco(InAsP)(μm)</th>
<th>λco(InGaAs)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>5.8947</td>
<td>-0.430.12</td>
<td>1.02</td>
<td>1.87</td>
<td></td>
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<tr>
<td>B</td>
<td>5.9199</td>
<td>-0.710.25</td>
<td>1.15</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5.9267</td>
<td>-0.97</td>
<td>0.29</td>
<td>1.20</td>
<td>2.11</td>
</tr>
</tbody>
</table>

Eg = energy bandgap

Id = dark current (at -30V bias)

VB = breakdown voltage (at 10 μA dark current)

a = lattice parameter
da/a₀ = (a₀ - a_epi)/a₀ = lattice mismatch between epi layer and substrate(a₀)

λco(InAsP) = longest wavelength absorbed by the InAsP (=1.24/Eg)

λco(InGaAs) = longest wavelength absorbed by the InGaAs whose lattice parameter is equal to that of the InAsP.
The devices were probe tested in wafer form to characterize dark current, breakdown voltage, and avalanche behavior with and without light. Table 2 summarizes device results obtained with three different wafers. Gains as high as 40 were observed with wafer C: the InAs$_{29}$P$_{71}$ alloy whose lattice parameter nearly matches that of low bandgap In$_{7}$Ga$_{3}$As, which would absorb 2.1 $\mu$m light. The three wafers all exhibited good p-n junction properties, having 50-80V breakdown voltages at -30V bias. Avalanche gain was observed on all devices.

Figure 3 contains dark current and gain characteristics of wafer A (InAs$_{12}$P$_{88}$ whose lattice constant would nearly match that of low-bandgap In$_{6}$Ga$_{4}$As, which would absorb light out to 1.87 $\mu$m). The low dark currents (0.7 nA @ -10V) and smooth gain characteristics are evident. The reverse-bias currents under dark ($I_d$) and white light illumination ($I_l$), as well as the calculated avalanche gain, are plotted semi-logarithmically as a function of the reverse-bias voltage, $V_r$. The dark current is constant at 0.5 nA up to biases of about 40V, above which it increases rapidly with increasing reverse bias, presumably due to avalanche multiplication. Under whitelight illumination from the topside, or p-side of the diode, the current, $I_r$, increases to about 100 nA at biases below 40 V. At biases greater than about 40 V, it increases rapidly as the result of avalanche gain.

<table>
<thead>
<tr>
<th>wafer#</th>
<th>$\lambda_{co}$ ((\mu)m)</th>
<th>$E_g$ (eV)</th>
<th>$I_d$ (@-30V) (nA)</th>
<th>$V_B$(@10(\mu)A) (V)</th>
<th>gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.02</td>
<td>1.22</td>
<td>0.5</td>
<td>80</td>
<td>10-40</td>
</tr>
<tr>
<td>B</td>
<td>1.15</td>
<td>1.09</td>
<td>10</td>
<td>50</td>
<td>10-100</td>
</tr>
<tr>
<td>C</td>
<td>1.20</td>
<td>1.03</td>
<td>50</td>
<td>60</td>
<td>10-40</td>
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</tbody>
</table>

We calculated the approximate avalanche gain, $g_a$, from the expression:

$$g_a = (I_l - I_d)/100$$

which is the difference between the diode current under illumination and in the dark, divided by the same difference at biases less that 40 V, namely 100 nA. As shown in Figure 3, $g_a$ is unity at voltages below 40 V, and increases rapidly to a value of 40 at 80 V, the highest reverse-bias
voltage the diode would sustain before becoming unstable. Gains of 10 can be achieved at biases of 70 V, at which the diode's reverse-characteristic is stable.

These initial results indicate that avalanche gain can indeed be obtained in InAs_{1-y}P_{y} whose underlying layers contain misfit dislocations (as evidenced by the surface cross-hatch pattern). The devices also exhibit reasonably low dark currents, a necessary condition for low noise devices. Future experiments will be conducted with InAs_{4}P_{6} layers and finally on InAs_{4}P_{6} structures topped with In_{7}Ga_{3}As. This layer absorbs light out to 2.1 μm and would create carriers, which would be swept into the InAs_{4}P_{6} region for subsequent avalanche gain.

In conclusion, we have demonstrated that low dark current and high avalanche gain can be achieved in InAs_{29}P_{71} p/n junctions grown directly on p-InP substrates with nearly 1% lattice-mismatch. This material has the same lattice parameter as In_{7}Ga_{3}As which would absorb light out to 2.1 μm and suggests that it may indeed be possible to construct a 2.1 μm APD using lattice-mismatched layers of InAsP deposited directly onto InP substrates without grading.

We gratefully acknowledge the support of the Ballistic Missile Defense Organization and the Office of Naval Research (Dr. A.M. Goodman, Technical Monitor) under a Small Business Innovation Research program.
$\text{epi}$

$n^\prime$: $\text{InAs}_y\text{P}_{1-y}$

$a > a_0$

$\approx 3 \mu m$

$p^\prime$: $\text{InP}$  substrate  $a_0 = 5.8694\,\text{Å}$
Figure 1. Desired structure for avalanche gain at 2.1 μm.

Figure 2. Actual avalanche photodiode structure used in this study.

Figure 3: Reverse-bias characteristics of an InAs$_{12}$P$_{88}$ avalanche diode.
References


SBIR Quarterly Review - Fourth Quarter 1994

Preparer: GHO

Name: InAsP/InGaAs Materials Development for 2.1 μm APDs
SUI Contract Number: C006
Agency: Office of Naval Research/SDIO
Contract Number: N00014-93-C-0254
Monitor: Dr. Alvin Goodman - (703) 696-4845
Principal Investigator: Dr. Gregory H. Olsen
Consultant(s): RUM/RF
Key Personnel: GHO, MJL, MJC, EM,
Start Date: 20-Sep-93
End Date: 20-Sep-95

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</table>

Percent Completion: 24 months 15 months 63%

Goal: Demonstrate a 2.06 μm avalanche photodiode with gain >5

Overall Status: Good.

Progress during Quarter: Good progress with abrupt lattice-mismatched InAsP layers (no grading). Low leakage, high gain. Complete wafer with InGaAs is being processed. EPI did good job on epi layers.

Current Problems: Poor performance of final structure. Still have plenty of time.

Outlook: Good. Another real first if we make it. A ready commercial market.

Future plans: Increase spending. Do more complete structures.

Consultant Work: Consultants are undercharged. Do we have a spatial scanning system?
SUBJECT: Distribution Statements on Technical Documents

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   QUARTERLY REPORT #5
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   DEVELOPMENT FOR 2.1 um
   AVALANCHE PHOTODIODES

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DEPUTY DIRECTOR
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