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PHASE I FINAL REPORT

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" ATOMIC LAYER CHEMICAL VAPOR DEPOSITION  
OF  $Al_xGa_{1-x}N$  for SOLAR BLIND UV-DETECTORS "

CONTRACT NUMBER N0014-87-C-0841  
SUBMITTED TO OFFICE OF NAVAL RESEARCH

RESTRICTION STATEMENT A

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## Phase I Final Report

### 1.0 Background

APA Optics completed an SDI supported Phase I SBIR program aimed at developing  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  materials technology using atomic layer epitaxy. The key objective of the Phase I work was to study the nitrogen vacancy problem using a unique switched atomic layer MOCVD approach as the growth technique. These nitrogen vacancies result in extremely high ( $10^{18}/\text{c.c.}$ ) carrier densities in single crystal epitaxial layers of GaN thereby rendering the material unusable for emitters (such as electroluminescent devices) or detectors (such as photoconductors or Schottky barriers).

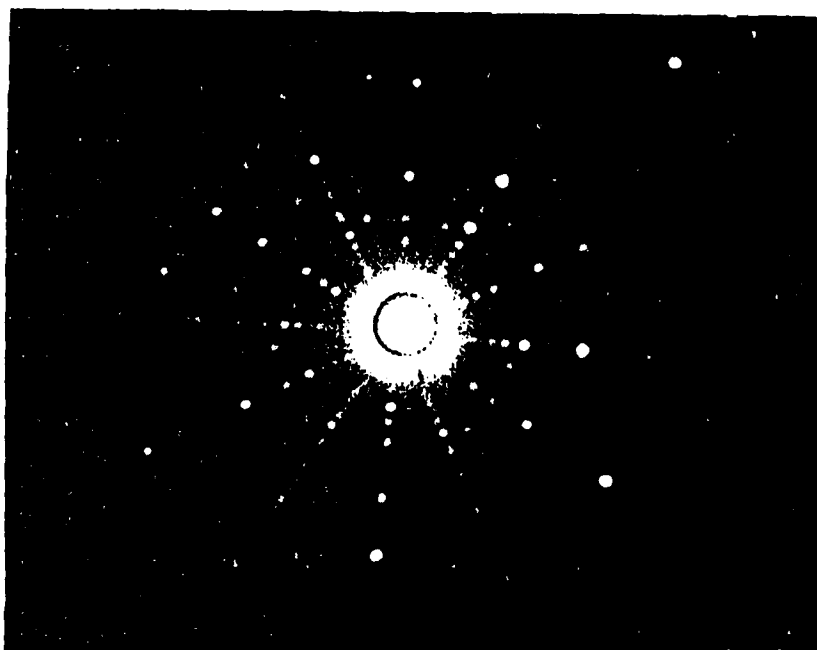
Four tasks were completed under Phase I program. Under the first task we designed and incorporated a unique SiC coated graphic substrate in our low pressure MOCVD system. This susceptor was designed to implement the switched atomic layer epitaxy approach. Program Task 2 focussed at growing single layers of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  (over entire 'x') using a standard low pressure MOCVD approach. We were successful in growing high quality single crystal layers. These layers were checked for single crystal nature (using Laue and RHEED), carrier concentrations and mobilities (using Van der Pauw and Hall measurements) and optical transmissions. These data as shown in Figures 1 (see next page), 2 and 3 indicate material growth matching some of the best reported values in literature.

| No    | Growth Temp. | Ga Flux% | NiI <sub>3</sub> Flux% | Growth Rate $\mu/\text{hr.}$ | Carrier Conc. $10^{18}/\text{cm}^3$ | Mobility 300K $\text{cm}^2/\text{V-sec}$ | Morp      |
|-------|--------------|----------|------------------------|------------------------------|-------------------------------------|------------------------------------------|-----------|
| 1-5   | 900          | 50       | 20                     | 0.67                         | 5-8                                 | 70                                       | Good      |
| 2-10  | 900          | 50       | 20                     | 0.5                          | 4-3                                 | 108                                      | Good      |
| 3-12  | 900          | 50       | 20                     | 0.5                          | 3.0                                 | 114                                      | Good      |
| 4-20  | 800          | 50       | 20                     | 0.49                         | 2.6                                 | 61                                       | Very Good |
| 5-21  | 800          | 25       | 20                     | 1.35                         | 3-6                                 | 39                                       | Fair      |
| 6-22  | 850          | 25       | 20                     | 0.25                         | 6.5                                 | 94                                       | Good      |
| 7-30* | 750          | 50       | 20                     | 0.43                         | 10.0                                | 79                                       | Fair      |

Figure 2. Experimental Results of GaN Growths at Different Temperatures



AlN



GaN



|                    |                       |   |
|--------------------|-----------------------|---|
| Accession For      |                       |   |
| NTIS               | ORASI                 | ✓ |
| DTIC               | TAB                   | ✓ |
| Unannounced        |                       | ✓ |
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Figure 1. Laue Patterns for an AlN and GaN Sample.

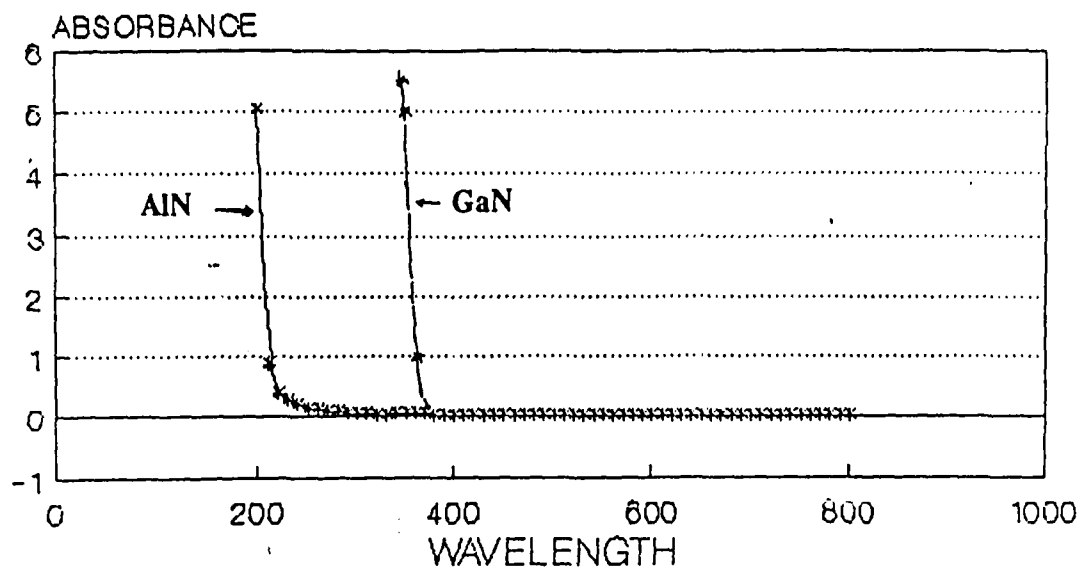


Figure 3. AlN and GaN Absorbance as a Function of Wavelength.

Under Task 3 we deposited GaN using an atomic layer epitaxy approach. With conventional atomic layer epitaxy we were able to reduce the single crystal epitaxy temperature for GaN to 775°C (compared to 850-950°C for conventional MOCVD. Please refer to Table 1). Subsequently we studied the nitrogen vacancy problem using a unique switched ALE approach. These experiments and resulting data will be described in much more detail in section 3. Based on these data we were able to conclusively show that single crystal epitaxy of GaN even at a temperature of 775 degree C suffers from the creation of nitrogen vacancies. These clearly point to the necessity of further decreasing the single crystal epitaxy temperature and providing a nitrogen plasma over the growth surface.

| No.  | Growth Temp. | Growth m/hr. | Ga Tube Ht. (in) | NH3 Tube Ht. (in) | Carrier Conc. /cc  | Mobility | Morphology |
|------|--------------|--------------|------------------|-------------------|--------------------|----------|------------|
| 1-24 | 775          | 3.7          | 5/16             | 5/16              | $4 \times 10^{18}$ | 18       | FAIR       |
| 2-26 | 775          | 1.2          | 1/2              | 1/8               | $2 \times 10^{19}$ | 163      | FAIR       |
| 3-32 | 775          | 1.5          | 1/2              | 1/4               | $2 \times 10^{19}$ | 90       | FAIR       |
| 4-34 | 775          | 1.5          | 1/2              | 1/8               | $3 \times 10^{19}$ | 43       | GOOD       |

Table 1. Summary of results of the atomic layer epitaxy experiments to date.

Task 4 of our program was aimed at laser assisted atomic layer epitaxy. However due to a late program start we were only able to complete the design and fabrication of the chamber cover necessary for injecting UV-light over the growth surface. We plan to do more work on UV-excitation for producing the nitrogen plasma in the Phase II program.

## 2.0 Results Summary

The following is a summary of key results obtained during the Phase I program.

1. We successfully deposited single crystal layers of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  over 1" sapphire substrates with thickness uniformities better than  $\pm 10\%$  using low pressure MOCVD as the growth technique.
2. We were able to grow extremely high quality single crystal layers of GaN with carrier concentrations of  $1 \times 10^{18}/\text{c.c.}$  and mobilities as high as 173.
3. We successfully grew single crystal epilayers of GaN at a rate of  $5.5 \text{ \AA} / \text{cycle}$  (approximately 1 atomic layer) using atomic layer MOCVD. To the best of our knowledge this is the first ever atomic layer growths of the AlGaIn material system.
4. Using switched atomic layer epitaxy, we successfully deposited single crystal GaN layers over Sapphire substrates (with AlN buffers) at growth temperatures as low as 775 degrees C. To the best of our knowledge these are the lowest reported MOCVD growth temperatures for GaN single crystal epitaxy.
5. We successfully correlated the nitrogen vacancies (carrier concentrations) in epitaxial GaN layers to the dead time between successive atomic layer growths. This to the best of our knowledge is the first direct evidence of a correlation between nitrogen vacancies and the high carrier concentrations observed in GaN layers.
6. We successfully fabricated some rudimentary photoconductive detectors on  $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$  layers. The responsivity of these detectors was measured using an excimer laser operating at 193 nm. These detectors showed no significant response to visible and IR radiation.

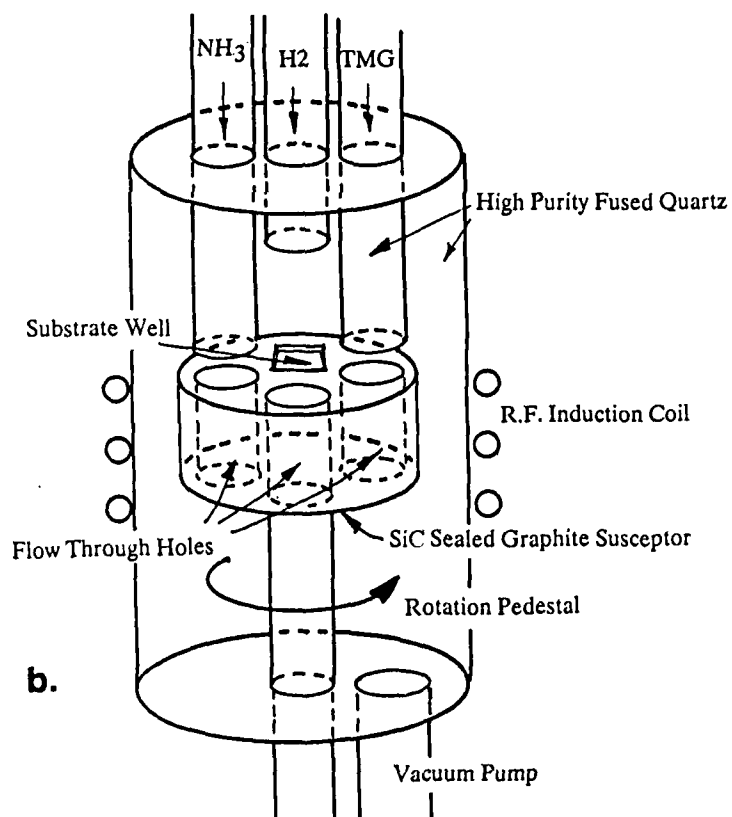
## 3.0 Technical Details

As described in our first technical report we are capable of directing  $\text{NH}_3$  and triethylgallium to our ALE susceptor via high purity fused quartz tubes (please see figure 4)

For the switched ALE - MOCVD experimentation the TEGa tube was placed at 1" from the susceptor (and hence the growth surface). We also determined that due to flows in excess of 1L/min,  $\text{NH}_3$  reaches essentially the entire susceptor once the height of  $\text{NH}_3$  tube is raised higher than about 1".

A controlled experiment was then carried out. It consisted of precleaning  $\text{Al}_2\text{O}_3$  substrates using procedures described in the first technical report. A buffer AlN epilayer

a.



b.

Figure 4a, Photograph of the ALE Susceptor. 4b, ALE Susceptor in the LP - MOCVD Chamber.

approximately  $0.2\mu$  thick was then deposited on these using low pressure MOCVD. The growth conditions were identical to those used for our standard AlN growths as described in our last technical report. These buffer AlN samples were then subsequently used as the growth substrates for switched atomic layer epitaxy experimentation.

In the switched ALE experiment the chamber was maintained at 76 torr. A constant ammonia flow of 1L/min and a hydrogen flow of 500 sccm was used for all the experiments. GaN layers were then grown by moving the (buffered AlN) sapphire substrate under the TEGa flux (12.5 sccm). The Ga flow was kept on for four seconds and switched off for four seconds and this cycle was repeated to accumulate a total growth thickness of  $0.4\mu\text{m}$ . This implies a growth thickness of  $5\text{\AA}$  (1 atomic layer) per cycle.

In subsequent experiments the off time was increased to 8, and 16 seconds. GaN epilayers were also grown with no off time (our standard growths). The following Table 3 summarizes the growth and characterization results.

| Run# | TEGon<br>Time, secs. | TEG off<br>Time, secs. | # cycles             | $n/\text{cm}^3$ at 300K | $\mu$ (300K) |
|------|----------------------|------------------------|----------------------|-------------------------|--------------|
| 1.   | 4                    | 4                      | 780                  | $4 \times 10^{19}$      | 47           |
| 2.   | 4                    | 8                      | 780                  | $5 \times 10^{19}$      | 43           |
| 3.   | 4                    | 16                     | 780                  | $9 \times 10^{19}$      | 18           |
| 4.   | 1                    | 0                      | continuous<br>growth | $2 \times 10^{18}$      | 114          |

*Table 2: results of Switched Atomic Layer Epitaxy Growths.*

One way of explaining the results is the realization that during the nongrowth cycle the GaN sample sits under an ammonia flux of 1L/min at 775 degrees C and 76 torr. Under these conditions nitrogen vacancies are still generated. Therefore the higher the off time the more the nitrogen vacancies and hence the larger the carrier concentrations. A deterioration of mobilities is also clearly indicated. These data are plotted in Figure 5. These data clearly point out the need for yet lower epitaxy temperatures which implies a nitrogen source other than ammonia. Nitrogen vacancy formation should also be suppressed by the use of excitation (such as a UV - Laser) for breaking the nitrogen (NH or N<sub>2</sub>) bonds. These are the approaches we are proposing for the program Phase 2.

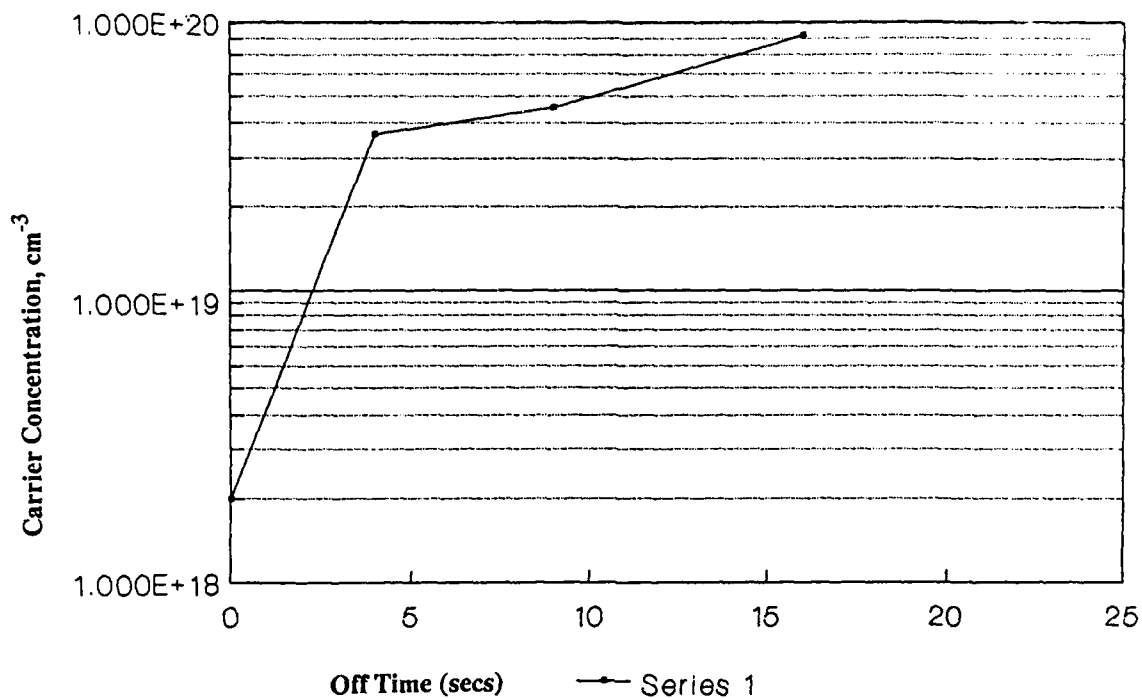


Figure 5. Variation Of Carrier Concentration (nitrogen Vacancies) With Off Time During Switched Atomic Layer Epitaxy.

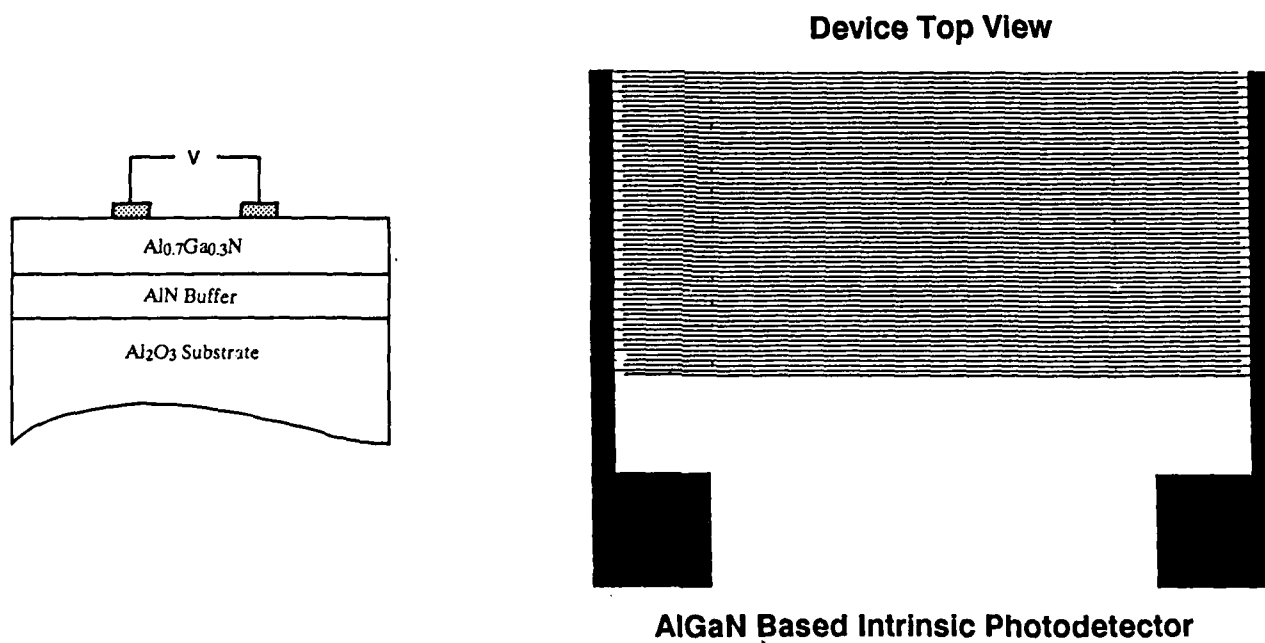


Figure 6. Photoconductive Detector Device.

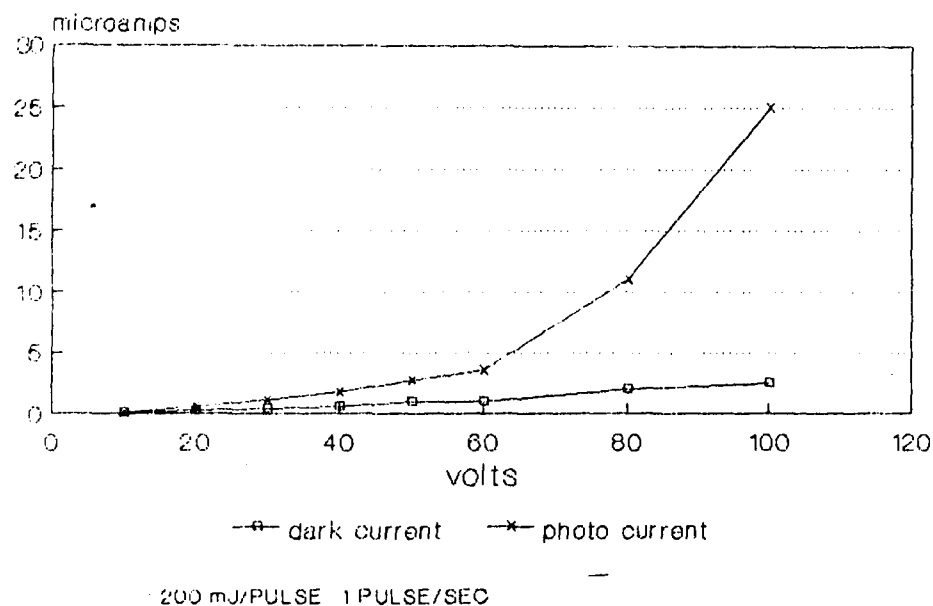
## Photodetector Fabrication and Testing

To check quality of growth we fabricated some simple photoconductive detectors. The device structure (with layers shown in Figure 6) consisted of an active layer of  $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$  grown on a buffered AlN layer which itself is grown on a basal plane  $\text{Al}_2\text{O}_3$  substrate. The device structure consists of interlaced finger electrodes. These electrodes occupy an area of 1 square mm. and each finger is  $3\mu$  wide with a  $3\mu\text{m}$  spacing. The electrodes are sputtered layers of TiW/Au approximately  $2000\text{\AA}$  thick. The electrode pattern is transferred to the device layers via a photolithographic lift off process.

Post fabrication the current voltage characteristics were measured for the device. The linearity of these characteristics indicates an ohmic contact and hence a photoconductive behavior. Subsequently the short circuit photocurrent was measured across the device as a function of bias voltage. The bias voltage varies from 0 to 100 V. As expected, no photocurrent is detected for 0 or very low voltages. We used a pulse excimer laser operating at 193 nm as the photon source. Each pulse was approximately 200 nsec mode. In Figure 7 we have plotted the photocurrent as a function of bias voltage. The two curves are for cases when 1 pulse/sec and 20 pulses/sec are incident on the device. Each pulse has an energy of 200 m joules.

In conclusion, we have successfully grown single crystal  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  layers using switched atomic layer MOCVD. We have also demonstrated some rudimentary photoconductive sensors based on  $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$  epitaxial layers.

a. PHOTO-CURRENT  
SAMPLE #59 AIN



b. PHOTO-CURRENT  
SAMPLE #59 AIN

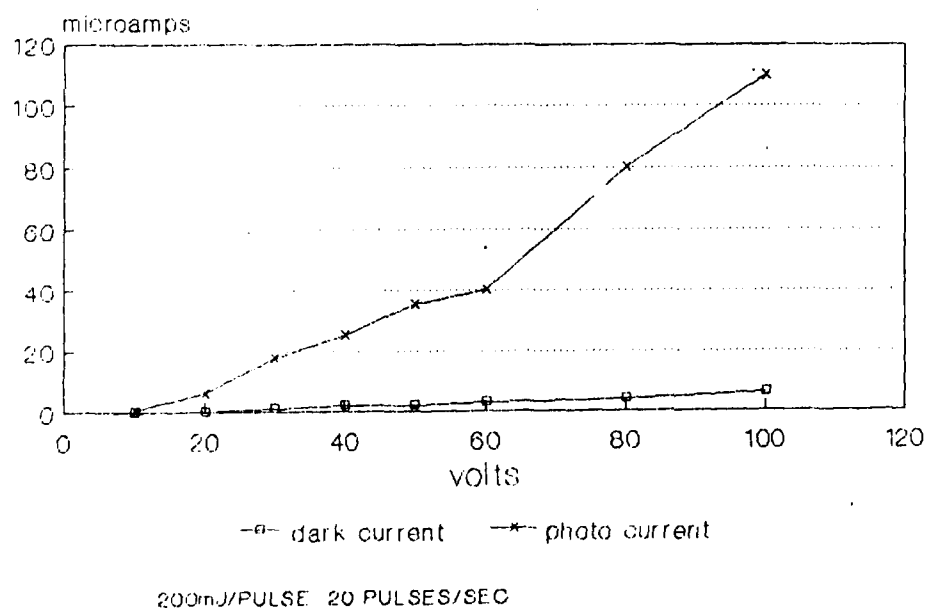


Figure 7a & 7b. Photo - Current as a Function of Bias Voltage For a Photoconductive Sensor.