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Low-Band-Gap, Amorphous-Silicon-Based Alloys by Chemical Vapor Deposition

Annual Subcontract Report 1 October 1985 - 31 January 1986

B. N. Baron
S. C. Jackson
Institute of Energy Conversion
University of Delaware
Newark, Delaware

Prepared under Subcontract No. XL-5-04074-3

SERI

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401-3393

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SUMMARY

Objectives:

The purpose of this research is to determine the potential of photochemical vapor deposition for producing high quality low band gap amorphous silicon germanium alloys for use in high efficiency multijunction thin-film photovoltaic solar cells.

Discussion:

Research on photochemical vapor deposition of a-$Si_{1-x}Ge_x$:H alloys has been carried out under four tasks - photo-CVD reactor, film deposition, materials characterization, and device fabrication. A photo-CVD reactor for mercury sensitized photolysis of silane-germane and disilane-germane mixtures was developed. The reactor features a UV transparent moveable Teflon curtain which eliminates deposition on the reactor window. UV light is provided by a low pressure mercury grid lamp.

Alloy thin films of undoped a-$Si_{1-x}Ge_x$:H with $0 \leq x \leq 1$ were deposited using mercury vapor mixed with SiH_4 or Si_2H_6, GeH_4 and diluent gas of Ar, He or H_2. Substrate temperatures ranged from 200-280°C. Alloy films 0.2-0.5 μm thick were deposited at rates up to 0.8 A/sec. A quantitative photo-CVD reactor model which accounts for spatially dependent photogeneration of gas phase

precursors, diffusing and film properties predicts the dependence of growth rate on reactor conditions leading to higher growth rate without window fouling.

Materials properties were characterized by measurements of Ge content, optical transmission and reflection and dark and photo conductivity. Ge content was found to depend primarily on gas feed composition. The optical gap for $a\text{-}Si_{1-x}Ge_x{:}H$ was found to range from 1.8 eV for x=0 to 1.05 eV for x=1.

The activation energy for dark conductivity was approximately half the optical gap, indicating that the material is intrinsic. Dark conductivity was found to increase with decreasing gap. The excess conductivity ($\sigma_p = \sigma_p - \sigma_d$) was nearly constant for material with optical gap less than 1.4 eV and was only 3 to 5 times lower than for high quality a-Si:H. Maximum photoconductivities were $\sigma_p > 10^{-6}$ S/cm. Hydrogen dilution and the absence of argon improved film properties. P-i-n photovoltaic devices, with i-layer optical gap of 1.35 eV, were fabricated using photo-CVD.

Conclusions:

- Low band gap $a\text{-}Si_{1-x}Ge_x{:}H$ alloys with $0 \leq x \leq 1$, $1 < Eg < 1.9$ eV and $\sigma_p > 10^{-6}$ S/cm have been deposited by photo-CVD.

- Opto-electronic properties of photo-CVD a-$Si_{1-x}Ge_x$:H are comparable to glow discharge and sputtered materials.

- P-i-n solar cells with low bandgap i-layers have been fabricated using photo-CVD.

- Optimization of photo-CVD of a-$Si_{1-x}Ge_x$:H is expected to lead to device quality low band gap material for high efficiency multi-junction thin film solar cells.

PREFACE

This research project is the result of a Solar Energy Research Institute initiative in New Ideas for Photovoltaic Conversion. The University of Delaware has invested significant resources in the laboratory facilities and equipment needed to perform the research. Lincoln University's participation as a lower-tier subcontractor has lead to involvement of faculty and students in photovoltaic research.

The interest and support shown by the Solar Energy Research Institute Solar Electric Division deserve special recognition. Collaboration between this project and work being carried out under SERI Subcontract XB-4-04061-1, which has proven to be invaluable, was encouraged from the beginning.

CONTRIBUTORS

The following personnel at the Institute of Energy Conversion, Lincoln University and the Solar Energy Research Institute have contributed to the work described in this report:

Principal Investigator	B. N. Baron
Reactor Design	S. C. Jackson R. E. Rocheleau W. A. Buchanan P. Wilson* R. Tullman S. Beard
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TABLE OF CONTENTS

SECTION 1.0

INTRODUCTION

A promising technical option for achieving high efficiency thin-film solar cells is the multijunction stacked solar cell. Multijunction cells using hydrogenated amorphous silicon germanium alloys (a-SiGe:H) with band gaps less than 1.5 eV for the low band gap cell have predicted conversion efficiencies over 15% (1). Much research effort is being devoted to preparation and characterization of a-SiGe:H (2) and a-SiGe:H,F (3) films made by glow discharge deposition.

An innovative approach for deposition of amorphous silicon materials is photochemical vapor deposition. There are several reports of photochemical vapor deposition of a-Si:H. These include direct photolysis at 185 nm using disilane (4) and mercury sensitized photolysis at 254 nm using silane (5) and disilane (6). Recently, photo-CVD of a-SiGe:H films from mixtures of germane plus silane (7) and germane plus disilane (8) have been reported.

The objective of this research is to determine the potential of solar cell quality low band gap a-SiGe:H films prepared by photochemical vapor deposition. Following the work of Konagai et al. (7), mercury sensitized photolysis of germane-disilane mixtures was selected for study.

In this report we describe an improved photochemical vapor deposition reactor that uniquely overcomes the problem of deposition on the reactor window. Deposition and characterization of a-$Si_{1-x}Ge_x$:H films with $0 \leq x \leq 1.0$ and, $1.0 \leq Eg \leq 1.88$ and preliminary device results are described.

SECTION 2.0

TASK 1 - PHOTO-CVD REACTOR

The photo-CVD reactor used in this work is shown schematically in Figure 1. This reactor is a significant improvement of the mobile transparent window or curtain described by Peters and Gebhart (10). The curtain shown in Figure 1 separates the reactor into two chambers. Deposition on the window is eliminated by locating the window in the chamber separated from the reactant gases and by flowing inert or reaction inhibiting gases through the window chamber. The reactant gas mixture flows through the lower chamber over a set of temperature controlled substrates. Other details of individual components have been described before (9).

Institute of Energy Conversion's
Photo - CVD Reactor

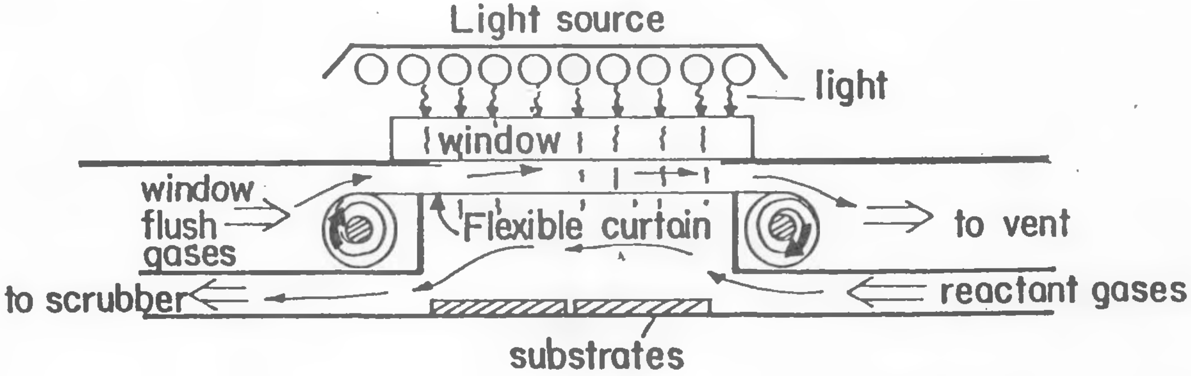


FIGURE 1

SECTION 3.0

TASK 2: a-$Si_{1-x}Ge_x$:H FILM DEPOSITION

Amorphous silicon-germanium alloy films were deposited in order to reproduce previously reported(1) depositions, and to extend the film composition to higher germanium content (50-100% Ge). The deposition parameters included those previously reported plus conditions which yielded higher growth rates and higher germanium content in the films. These deposition conditions are summarized in Table 1.

In order to achieve the higher germanium content and higher growth rates, the reactor operation had to be optimized in order to overcome a problem with a slight amount of window fouling that occurred. This problem was noted previously (9). Modifying the mercury bubbler and operating it at a lower temperature allowed for a lower mercury concentration in the feed gas (Run #94 and later). As a result, absorption of the light and generation of the gas phase film precursors occurs closer to the substrate and further from the curtain and the curtain seal. A higher growth rate (~0.8 A/sec) was obtained with less curtain and window fouling. This behavior was predicted by the photo-CVD reactor model discussed in Section 6.0.

TABLE 1: DEPOSITION CONDITIONS

RUN NUMBER LAYER	FEED GAS COMPOSITION*	SUBSTRATE TEMP, °C	Hg BUBBLER TEMP, °C	REACTOR PRESSURE TORR	Si_2H_6 FLOW SEEM	GeH_4 FLOW SEEM	SiH_4 FLOW SEEM	OTHER DILVENT**		Dopant +	$SiCH_6$	NOTES
084-i	17	240	30	13	0.7	0.30	0	5.7	Ar			
086-i	25	240	30	13	0.6	0.44	0	8.36	Ar			
094-i	17	240	30	13	0.7	0.30	0	5.7	Ar			Dropped [Hg] by ~ x 10^{-3}
098-i	17	240	30	11	0.7	0.30	0	5.7	He			" "
099-i	25	240	30	11	0.6	0.44	0	8.36	He			"
101-i	17	280	30	11	0.7	0.30	0	5.7	He			"
102-i	25	280	30	11	0.6	0.44	0	8.36	He			"
110-i	33	240	30	11	0	0.44	0.9	8.36	He			"
112-i	100	240	30	11	0	0.44	0	8.36	He			"
114-p	0	160	30	11	0	0	1.5	0.52	He	B_2H_6-.026	0.37	"
114-i	25	280	30	11	0.6	0.44	0	8.36	He	0	0	"
114-n	0	280	30	11	2.0	0	0	0.50	He	PH_3-0.022	0	"

* Feed Gas Composition = % GeH_4 /[GeH_4 + n·Si_n H_{2n+6}]

** <10% in Feed Gas

Alternate feed gas compositions were explored. H_2 dilution and substituting He for Ar as an inert gas lead to improved film properties. Substituting monosilane for disilane was used to obtain films with high Ge content (x>0.5).

SECTION 4.0

TASK 3 - FILM CHARACTERIZATION

Photo-CVD a-$Si_{1-x}Ge_x$ films were characterized by composition, optical absorption, dark and photo-conductivity and activation energy.

The germanium content, x, was determined by energy dispersive analysis of x-rays. This technique was calibrated with samples measured by electron microprobe analyses performed by C. Herrington at the Solar Energy Research Institute. The film composition was accurately measured using linear response factors. The germanium content, thickness, and deposition rate as shown in Table 2 are all higher than previously reported(9). The germanium content was predominately determined by the gas feed composition as shown in Figure 2 with only slight variations due to substrate temperature or inert gas dilution. The germanium is preferentially deposited in the film as shown in Figure 2. For example, a feed gas composition of 25% GeH_4 results in a film with a germanium content of 57 to 65%. This enrichment has been reported by others using glow discharge (Konagai et al. (13)). In the case of Hg sensitized photo-CVD, this preferential deposition may be explained by a larger quenching cross section of germane relative to mono or disilane.

Table 2: BASIC MATERIAL PROPERTIES

OF PHOTO-CVD a-$Si_{1-x}Ge_x$:H FILMS

Run #	Thickness (A)	Rate (A/sec)	Ge Content (%)
084	4200	0.6	53
086	4200	0.6	66
094	4800	0.7	51
098	3900	0.6	42
099	4000	0.6	57
101	4800	0.7	48
102	5400	0.8	64
110	4200	0.6	90
112	4800	0.7	100

As expected, the optical gap and film composition are closely correlated, Figure 3. At a constant substrate temperature, the relationship between film composition and optical band gap is approximately linear. The gap energy decreases with increasing substrate temperature. For example, for a film composition of ~45%, the Eg≃ 1.55 eV at 200°C, 1.46 eV at 240°C and 1.43 eV at 280°C. This trend has been reported by others including Mackenzie et al. (12) and has been attributed to the greater amount of hydrogen bonded in the films at lower temperatures.

The opto-electronic properties of a-$Si_{1-x}Ge_x$:H are shown as a function of feed gas composition in Figure 4. Previously reported(9) properties have been included in this figure for completeness. The optical gap (bottom curve) varies from ~1.8-1.9 eV for a-Si:H to 1.04 eV for a-Ge:H and is linear with the feed gas composition below 35% Ge. The activation energy is approximately half the optical gap energy indicating that the position of the Fermi level is near the middle of the gap. Data reported by Mackenzie et al. (12) is consistent with this observation.

The photo and dark conductivities are the top two curves in Figure 3. The light and dark conductivity of a-SiGe:H appear to show a minimum between 5 and 20% GeH_4 in the gas feeds and then increase as the GeH_4 concentration goes to 100%. Argon dilution and decreasing substrate temperature lowers both the light and dark conductivities at a fixed gas feed composition. The best photo-conductivities and corresponding dark conductivities below an optical gap of 1.6 eV are listed in Table 3. These conductivities almost equal the best reported by Konagai (10) but are at a lower Eg and a lower hydrogen dilution. At gas feed GeH_4 compositions greater than 10%, Figure 4, the dark conductivity increases sharply and is nearly equal to the light conductivity for amorphous Ge. This small ratio of light to dark conductivity at high Ge content may be due to the small activation energy of a-Ge:H (Eg=1.06eV) and the light intensity used in these measurements. This behavior has been observed by Rudder et al. (14) for amorphous silicon germanium alloys deposited using a dual magnetron sputtering system.

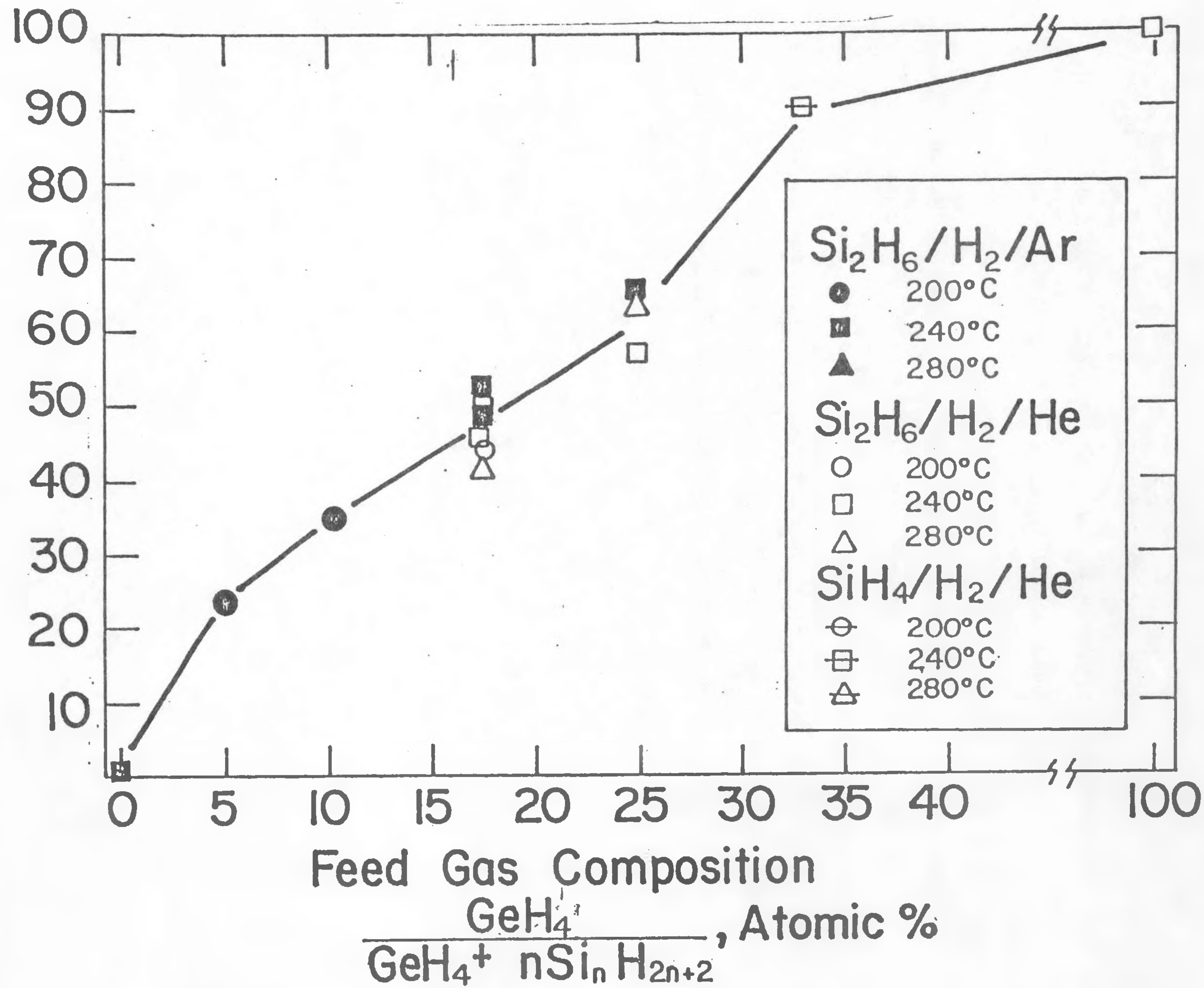
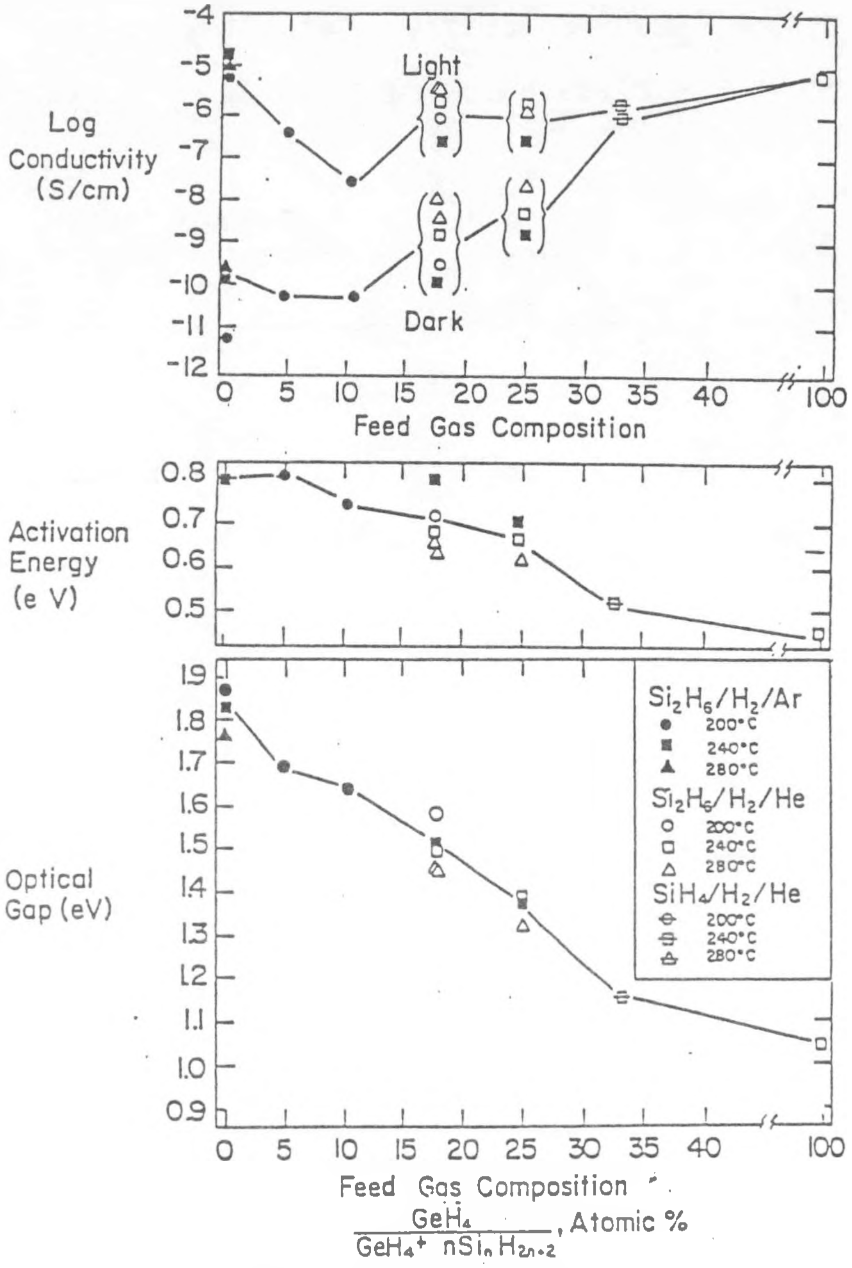


FIGURE 2: Germanium content in the film (measured by EDS) as a function of feedga composition and substrate temperature.

Figure 3
Opto-Electronic Properties of a-SiGe:H
Films Deposited from GeH_4 and Si_2H_6 or SiH_4



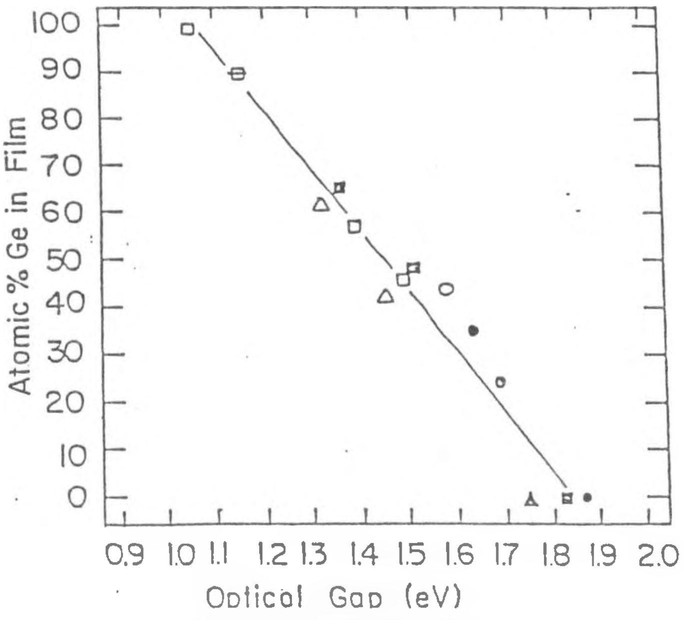


Table 3: THE BEST PHOTOCONDUCTIVITIES AND CORRESPONDING DARK CONDUCTIVITIES BELOW Eg OF 1.6 eV

Run #	Feed Gas Composition	Egap eV	σ_p S/cm	σ_d S/cm	Substrate Temp, °C	σ_p/σ_d	X Atomic % Ge
98	17	1.52	5.7×10^{-6}	1.1×10^{-9}	240	5.2×10^{3}	42
99	25	1.39	2.1×10^{-6}	6.5×10^{-10}	240	3.2×10^{3}	57
101	17	1.44	5.5×10^{-6}	1.2×10^{-9}	280	4.6×10^{3}	48
102	25	1.34	1.6×10^{-6}	4×10^{-9}	280	4×10^{3}	64
110	30	1.16	2.5×10^{-6}	1.1×10^{-6}	240	2.3	90
112	100	1.06	1.3×10^{-9}	1.1×10^{-9}	240	1.2	100

The photo-conductivities reported by Rudder, however, are an order of magnitude lower but may be due to their use of a different light source (He-Ne laser) for the photo-conductivity measurements. Other investigators including Weisz et al.(15) and Mackenzie et al.(12) have also reported a strong minimum in the photo-conductivity between 20 and 80% germanium film composition.

In summary, low band gap a-$Si_{1-x}Ge_x$:H films with: x-0.4-1.0; Eg = 1.5-1.0eV; Ea~1/2Eg; and $\sigma p > 10^{-6}$ S/cm have been deposited by mercury sensitized photo-assisted CVD from silane, disilane, and germane. Hydrogen dilution and the absence of argon in the reaction mixture substantially improves film properties.

SECTION 5.0

Task 4: Device Fabrication

Prototype low bandgap p-i-n devices with a-$Si_{1-x}Ge_x$:H (x - 0.63 and E_g = 1.35 eV) intrinsic layers were fabricated using photo-CVD. The substrate was tin oxide coated glass (Cherry Display, El Paso, TX). The p-layer was boron doped a-SiC:H. The i-layer thickness was 0.25 micron. Deposition conditions for the p, i and n layers are summarized in Table 1 (Run No. 114). Contact to the n-layer was provided by evaporated aluminum. Nine devices with area = 0.09 cm^2 were defined by photolithography and etching. Four devices were shorted. Five devices were unshorted and exhibited photovoltaic behavior.

The dark and light I-V behavior of a typical device from Run No. 114 are shown in Figure 4. The I-V curve under 87.5 mW/cm^2 ELH illumination was characterized by J_{sc} = 10.3 mA/cm^2; FF = 0.33; and V_{oc} = 0.36 V. current collection is strongly voltage dependent, i.e., J_L at -1.2 V was 15 mA/cm^2. The low V_{oc} and FF are also indicative of poor material quality. Subsequent investigation revealed that the reactor had developed an air leak at the time of Run No. 114. As seen in Table 1, Run 114 was done after the i-layer deposition studies.

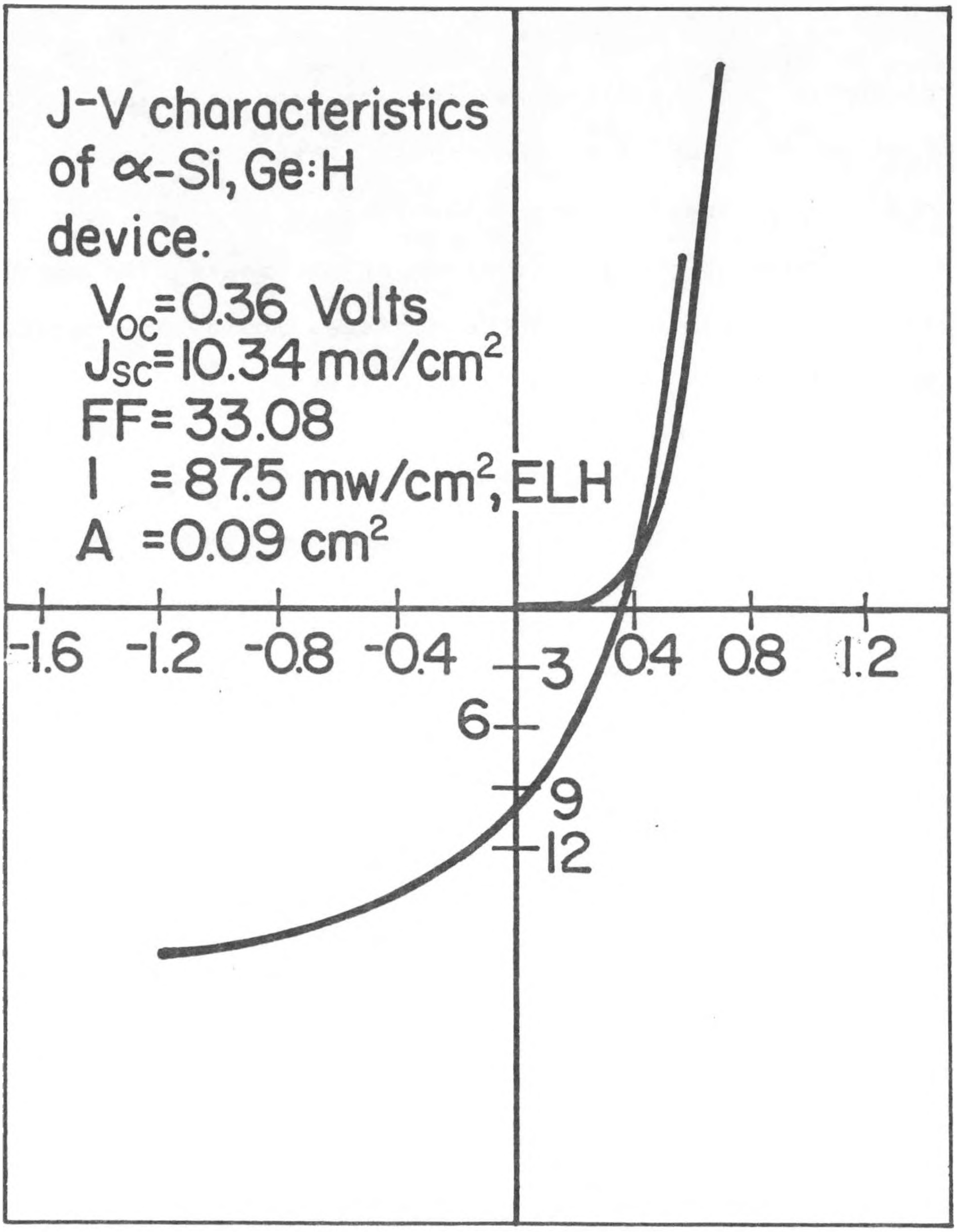

J-V characteristics of α-Si, Ge:H device.
V_{OC}=0.36 Volts
J_{SC}=10.34 ma/cm²
FF= 33.08
I = 87.5 mw/cm², ELH
A =0.09 cm²
-1.6
-1.2
-0.8
-0.4
0.4
0.8
1.2
3
6
9
12

Figure 4

SECTION 6.0

PHOTO-CVD MODEL RESULTS

A model(20) of the photo-CVD reactor was used to guide optimization of deposition conditions. This model quantitatively accounts for the speed at which the curtain is moved, the spatially dependent photo-generation of gas phase film precursors (16, 17, 18), their diffusion to surfaces inside the reactor, and their subsequent reaction to form film.

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ABSTRACT

Amorphous silicon-germanium alloy thin-films were deposited by mercury-sensitized photo chemical vapor deposition. Films were characterized by measurements of Ge content, optical absorption and conductivity. Intrinsic a-$Si_{1-x}Ge_x$:H with $0 \leq x \leq 1$, $1 < E_{opt} < 1.9$eV and $\sigma_p > 10^{-6}$ S/cm were obtained.