

# **Comprehensive Research on Stability and Performance of a-Si:H and Alloys**

## **Phase I Team Annual Technical Report, 31 May 1994 - 30 May 1995**

Vikram Dalal  
*Iowa State University*  
*Ames, Iowa*

NREL technical monitor: B. von Roedern



National Renewable Energy Laboratory  
1617 Cole Boulevard  
Golden, Colorado 80401-3393  
A national laboratory of  
the U.S. Department of Energy  
Managed by Midwest Research Institute  
for the U.S. Department of Energy  
under Contract No. DE-AC36-83CH10093

Prepared under Subcontract No. XAN-4-13318-08

August 1996

This publication was reproduced from the best available camera-ready copy submitted by the subcontractor and received no editorial review at NREL.

#### **NOTICE**

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available to DOE and DOE contractors from:  
Office of Scientific and Technical Information (OSTI)  
P.O. Box 62  
Oak Ridge, TN 37831  
Prices available by calling (423) 576-8401

Available to the public from:  
National Technical Information Service (NTIS)  
U.S. Department of Commerce  
5285 Port Royal Road  
Springfield, VA 22161  
(703) 487-4650



## **Preface**

This report represents the research work done under the first year ( Phase I ) of NREL subcontract XAN-4-13318-08. The work focussed on investigating device structures in a-Si:H alloys and on film growth in a-(Si,Ge):H materials, using ECR plasma conditions.

The investigators were:

Vikram Dalal, PI

Ralph Knox, Mohan Bhan, Kay Han, Robert Girvan, Sanjeev Kaushal, Scot DeBoer, E. X. Ping, J. Xu, L. Sipahi and F. Martin.

We wish to thank all the NREL a-Si team members for many fruitful discussions, and also want to express our appreciation to Werner Luft and Bolko Von Roedern of NREL for many useful and productive discussions. We are especially grateful to Dr. Rajeev Arya of Solarex for supplying us with tin oxide substrates, and for providing samples for testing and comparison.

# Table of Contents

Preface	i
Table of contents	ii
List of figures	iii
Executive summary	1
Chapter 1. Device Research in a-Si:H	2
Chapter 2. Research on a-(Si,Ge):H films	22
References	38

## Figure Captions

1.1	Schematic diagram of the reactor	3
1.2	Basic device structure	4
1.3	Plasma potential of a H-ECR discharge as a function of pressure and power	6
1.4	Inflexion point in device I(V) curve when an improper buffer layer is used	8
1.5	(A) Methane and diborane grading of p layer (B) Band diagram resulting from grading	9
1.6	Device I(V) curve of an ECR device deposited at 350 C. Al back contact is used.	11
1.7	Quantum efficiency , and quantum efficiency ratio, of the device in Fig. 1.6. The ratio is [QE at 0V/QE at +0.4 V]	12
1.8	Initial I(V) curve of ECR device used for stability measurements	15
1.9	Initial I(V) curve of Glow discharge device used for stability measurements	16
1.10	Quantum efficiency and QE ratio curve for ECR device whose I(V) curve was shown in Fig. 1.8	17
1.11	Quantum efficiency and QE ratio curves for GD device whose I(V) curve was shown in Fig. 1.9	18
1.12	Degradation in current, voltage and fill factor for the devices whose initial I(V) curves were shown in Fig. 1.8 and 1.9. The intensity of light soaking was 300 mW/cm <sup>2</sup> under ELH lamp illumination..	20
1.13	QE ratios of ECR and glow discharge devices after light soaking. The higher value for the ratio for the glow discharge device indicates poorer hole collection properties after degradation in GD compared to ECR material.	21

## Figures

2.1	Dependence of ion current on pressure in a H <sub>2</sub> -ECR plasma	24
2.2	Variation of electron temperature with pressure in a H <sub>2</sub> -ECR plasma	24
2.3	Variation of plasma potential with pressure in a H <sub>2</sub> -ECR plasma	25
2.4	Dependence of ion current on pressure in a He-ECR plasma	25
2.5	Dependence of electron temperature on pressure in a He-ECR plasma	26
2.6	Dependence of plasma potential on pressure in a He-ECR plasma	26
2.7	IR spectrum for an a-(Si,Ge):H film of Tauc gap 1.44 eV, deposited using H <sub>2</sub> -ECR discharge	27
2.8	H content in a-(Si,Ge):H films as a function of Tauc gap for films deposited using either He or H <sub>2</sub>	28
2.9	Tauc gap vs. Germanium content in films deposited using He and H <sub>2</sub> .	29
2.10	Photo-conductivity of a-(Si,Ge):H films as a function of Tauc gap, using either He or H <sub>2</sub> - ECR discharge.	31
2.11	Dark conductivities of films deposited using either He or H <sub>2</sub> .	32
2.12	Photo-sensitivity of films deposited using either He or H <sub>2</sub> .	33
2.13	Subgap absorption curve for a typical a-(Si,Ge):H film of 1.54 eV Tauc gap	34
2.14	Relationship between Subgap $\alpha$ , measured at the shoulder, and Tauc gap, for films deposited using either He-ECR or glow-discharge.	35
2.15	Relationship between valence band Urbach energy( $E_{uv}$ ) and Tauc gap for films deposited using either He-ECR or glow-discharge processes.	36

## Executive Summary

This report covers the research done during the first phase of the subcontract. During this period, we have concentrated on two areas: improving the voltage and stability of a-Si:H devices made using ECR deposition, and improving the properties of a-(Si,Ge):H films also using ECR deposition.

### 1. Device research on ECR-a-Si:H

During this period, we successfully solved the difficult problem of controlling B diffusion at high temperatures from p into i layers in superstrate devices ( where p layer is the first layer deposited on a transparent conducting oxide ). We used a grading scheme for the p layer which used grading of both C concentration and B concentration in the p layer to control both the band bending and diffusion of B from the p layer. Using this strategy has allowed us to increase our open circuit voltages to the 0.8 V range from the previous 0.75 V for devices deposited at 350-370 C, the range of temperatures that produced the most stable films. The fill factors remain in the 0.65-0.67 range, comparable to previous fill factors.

The quantum efficiency in the blue region remains low, and we have some work to do to optimize the p layer further to improve the QE and the voltage.

We have also studied the stability of our ECR devices against the stability of comparable devices made using glow discharge deposition. We were careful to keep voltages, the thickness of the i layer and fill factor comparable for both sets of devices, so that we can measure real changes in device performance. We found that the ECR devices appear to be more stable than glow-discharge devices in all three parameters[ current, voltage and fill factor]. An analysis of quantum efficiency in the devices after degradation reveals that the increased stability is directly related to the improved stability of the ECR i material as compared with the glow discharge i material.

### 2. Research on a-(Si,Ge):H films deposited using ECR technique

During this period, we have systematically studied the deposition of a-(Si,Ge):H films using remote, low pressure ECR techniques. We have used two gases, H<sub>2</sub> and He as the primary plasma-region gases. We found that the properties of the film depend upon which gas is used as the plasma gas. In particular, we find that the H content, and the Tauc bandgap, are much lower for the same Ge/Si ratio in the film when He is used as the plasma gas as compared to when H<sub>2</sub> is used as the plasma gas. The electronic properties, such as Urbach energies of valence band tails and midgap defect densities, are also better ( lower values ) when He is used. We have measured the properties of the plasma discharge generated with either of these gases, and we find that the plasma potentials and ion energies are higher for He than for H<sub>2</sub> plasma conditions. Therefore, we believe that significant ion bombardment when He is used may account for the lower H content and the better electronic properties. An interesting observation is that even for a-Si:H, the films produced using He as the plasma gas have a much lower H content, and a lower gap, than a film produced using H<sub>2</sub> as the plasma gas. This fact may be useful for doing some creative bandgap engineering in devices.

## Chapter I

### Device Research in ECR-a-Si:H

#### I.1 Review of Previous Work

##### A. Material Research

In the previous contract[1], we have shown that the use of remote, low pressure electron-cyclotron-resonance(ECR) plasma beam to deposit the a-Si:H material leads to a material which has both good electronic properties, and significantly better stability than standard glow-discharge deposited material. To recapitulate, the deposition technique consisted of exciting either  $H_2$  or He introduced upstream using a microwave-ECR source. The reactor is schematically shown in Fig. 1.1. The energetic beam of ions and radicals travels towards the substrate, and reacts with Silane introduced near the substrate through a separate nozzle. The silane reacts with the energetic beam, and decomposes primarily into silyl radicals, and then growth proceeds from the silyl radical. Since the pressure in the chamber is low(5-15 mT)the growing surface is subjected to bombardment by 10-15 V by the plasma-generated ions, and if H is the plasma gas, some etching-during-growth takes place. The combination of ion bombardment and etching leads to a film with a significantly improved stability, particularly when  $H_2$  is used as the diluent gas. Typically, the films are deposited at temperatures in the range of 300-360 C. To further improve stability, the films can be compensated at the sub-ppm level using diborane. We had shown that the addition of diborane led to improvements in both the initial and light-soaked defect densities in films which were deposited using  $H_2$ [2].

One of the observations we had made was that the Tauc gap of the material was a function of whether  $H_2$  or He was used as the plasma gas. The use of He seemed to lead to a lower Tauc gap(1.67 eV vs. 1.75 eV). During the course of this work, we have measured the H content of the films, using IR spectroscopy, and found that the films using He had a significantly lower H content(4-5%) than films made using  $H_2$  as the plasma gas(7-8%).[ See Ch. II for more details]. This observation will be very useful later on when we discuss the results on a-(Si,Ge):H in Chapter II.

##### B.Device development

During the previous contract, we had started initial device development. For reference, we are concentrating on superstrate type cells, using standard textured and untextured tin oxide/glass substrates. The substrates have been either purchased Asahi tin oxide with a low haze(6%), i.e. low texture, or textured tin oxide kindly provided by Solarex. The basic structure of the device is shown in Fig. 1.2. The cell consists of a *p* layer of a-(Si,C):H, followed by a buffer layer(I1), an *i* layer(I2), and the final *n* layer. All amorphous layers are deposited consecutively in the ECR reactor, with appropriate purging and in-situ cleaning of the reactor between layers. An Al contact completes the structure. We do not use a highly reflective ITO/Ag back contact, because our ITO/AG contact technology is not very reliable. In particular, we run into fill factor

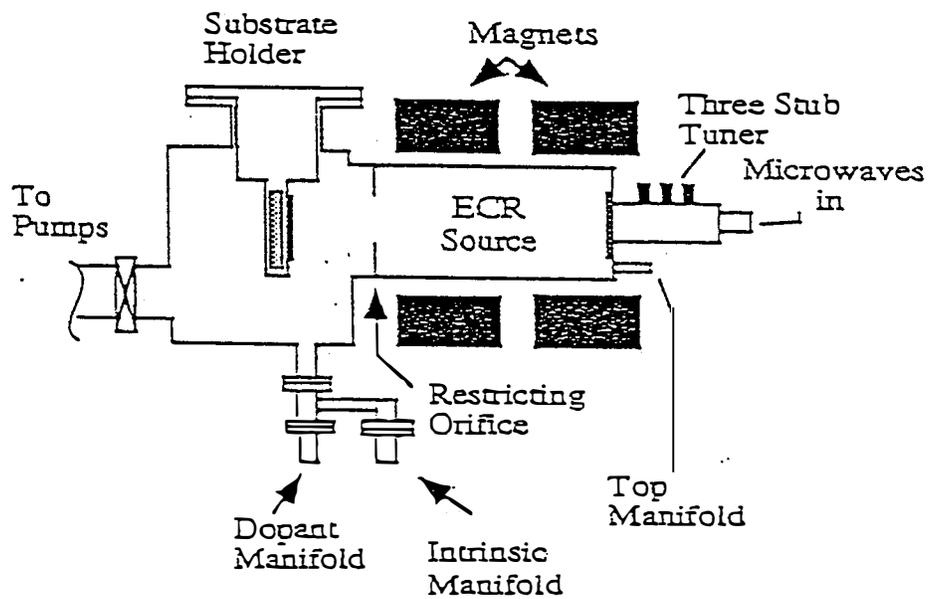


Fig. 1.1 Schematic diagram of ECR reactor. The resonance zone is about 25 cm. away from the sample.

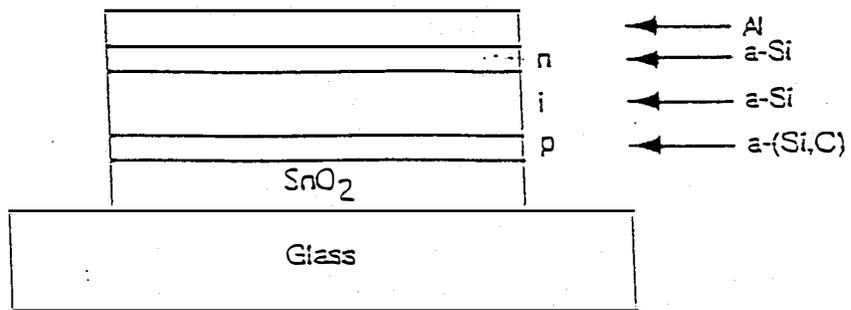


Fig. 1.2 Schematic diagram of the device structure

problems (ohmic contact) with such a contact, even though the contact does lead to significant increases in currents.

Using Al contacts, we had shown that we could obtain reasonable fill factors(63-64%) and voltages(0.75V) in cells deposited at 350 C, and somewhat higher voltages(0.8V) in cells deposited at 300 C, with the efficiency (initial) of the latter cell (300 C deposition) being in the 7-7.5 % region. We had made no measurements of the device stability in that cell, nor had we been very successful in routinely depositing good cells at 350-370 C, which are the temperature regimes that produced the most stable materials[2]. During the course of this work, we have concentrated on depositing cells with good fill factors at the same temperature that we deposit the best materials. We have also concentrated on studying how to increase the voltage from 0.75 V to 0.8 V, and on device stability, to see if the increased stability of materials translates into increased stability of devices. Note that we continue to use only H<sub>2</sub> diluted-i layers when making the cells. The cell development using He dilution of the i layer will be done in the future.

## I.2. Research on Devices

In this section, we describe our research on fabrication of superstrate devices in a-Si:H using low pressure, remote ECR deposition techniques.

Device development on superstrates using the new techniques presents peculiar challenges to a device designer. The previous device designs for glow-discharge depositions were optimized for much lower temperatures(200-250 C), and much lower plasma densities. In contrast, the material development we are working on requires high temperatures( 350-370 C), and high plasma densities.

The problems that we faced in making devices in this high temperature, high plasma density regimes were:

1. At higher temperatures, the H ions and radicals produced by the ECR beam reacted with the tin oxide substrate, reducing it to metallic tin, which would then diffuse through the device and reduce the performance[3]. This is a non-trivial problem even at low temperatures for ECR systems, because the plasma densities one deals with in the low pressure regime characteristic of the material deposition are very high(  $10^{10}/\text{cm}^3$  range or higher in the ECR zone). The high H flux, combined with the high H ion energies, leads to a rapid etching of tin oxide. As an example, in Fig. 1.3, we show the ion energies(plasma potential) incident on the substrate of a H-ECR plasma as a function of pressure in the reactor. It is obvious from these figures that the low pressure conditions can provide high fluxes and high energies to the substrate.

To overcome this problem, we make the p layer using He instead of H<sub>2</sub> as the plasma gas. With He, the only H present comes from the dilution gas of the diborane mixture, and from decomposition of silane and methane used to deposit the a-(Si,C):H. Also, with He, we can use a much lower power(100 W), and higher pressures(20 mT) than is the case with H plasmas, because the He metastable atom which is responsible for the fractionation of silane into silyl

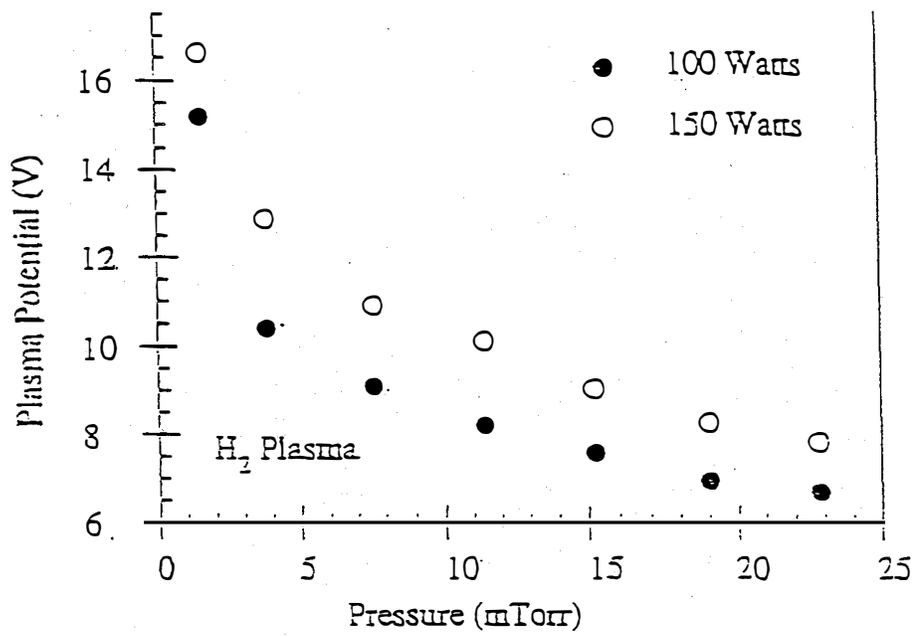


Fig. 1.3 Plasma potential in H-ECR discharge as a function of pressure and power

radical has a much longer mean free path than the H radical at a given pressure. We find that the combination of lower power and higher pressures allows us to deposit the p layers in a way which is compatible with the tin oxide substrate. To further make sure that we do not reduce tin oxide during the deposition of the p layer, we keep the temperature of the deposition low (about 190-200 C).

We also found that if we increased the temperature of the p layer (say to 300 C range), the open circuit voltages of the devices decreased precipitously. We believe this is a consequence of catalytic CVD of silane by diborane, a reaction whose rate increases as temperature increases. In such a case, one ends up with a low gap mixed B-Si layer, which probably creates problems at the p-i interface, leading to lower voltages.

To recapitulate, we have found that making p layers using He dilution and keeping the temperature of the p layer low during deposition allows us to make cells with higher voltages and reasonable fill factors. Typical flow rates of gases during the p layer depositions are:

$\text{SiH}_4 = 5 \text{ sccm}$

$\text{CH}_4 = 2 - 10 \text{ sccm}$  (Varies during growth of p layer, see below)

1%  $\text{B}_2\text{H}_6/\text{H}_2 = 20 \text{ sccm}$

The typical growth time for the p layer is 120 seconds.

2. Diffusion of B from the p into the i layer. For normal glow-discharge deposited p-i-n devices, diffusion of B is generally not a problem. Even when it is, using a buffer (I1) layer with a higher bandgap, e.g. using an a-(Si,C):H layer, between the p and the i layers avoids this diffusion problem[4]. One generally needs to use only small amounts of C in such a buffer layer, since the diffusion of B is not a severe problem at 200-250 C.

In contrast, in our case, the higher temperatures used for the i layer (350-370 C), create severe diffusion problems. While it was relatively easy to block B up to about 275-300 C using normal buffer layers, B diffusion became a major problem at higher temperatures.

Normal buffer layers just did not seem to work. We discovered early on that we needed more C in the a-(Si,C):H layer to block B diffusion; but such devices also sometimes tended to give inflexion points in the I(V) curve, as shown in Fig. 1.4[1]. We had previously described this phenomenon as being due to possible hole trapping at the p-i interface.[1].

To overcome this problem of B diffusion and interfacial trapping of holes due to non-matching of valence bands between either the buffer and the p layers, or the buffer and the i layers, we thought of using a tapered B profile in the p layer. What we do is to simultaneously reduce the bandgap of the p layer, and the B content, during the final stages of the p layer. See Fig. 1.5. By doing this, we achieve a graded gap that potentially enhances electron collection and also reduces B diffusion by reducing the B content in the source of diffusion.

After making the p layer, we thoroughly purge the reactor, using repeated purges with  $\text{N}_2$ . Then, a very thin high C, followed by repeated purges with Silane and Hydrogen. Then, we

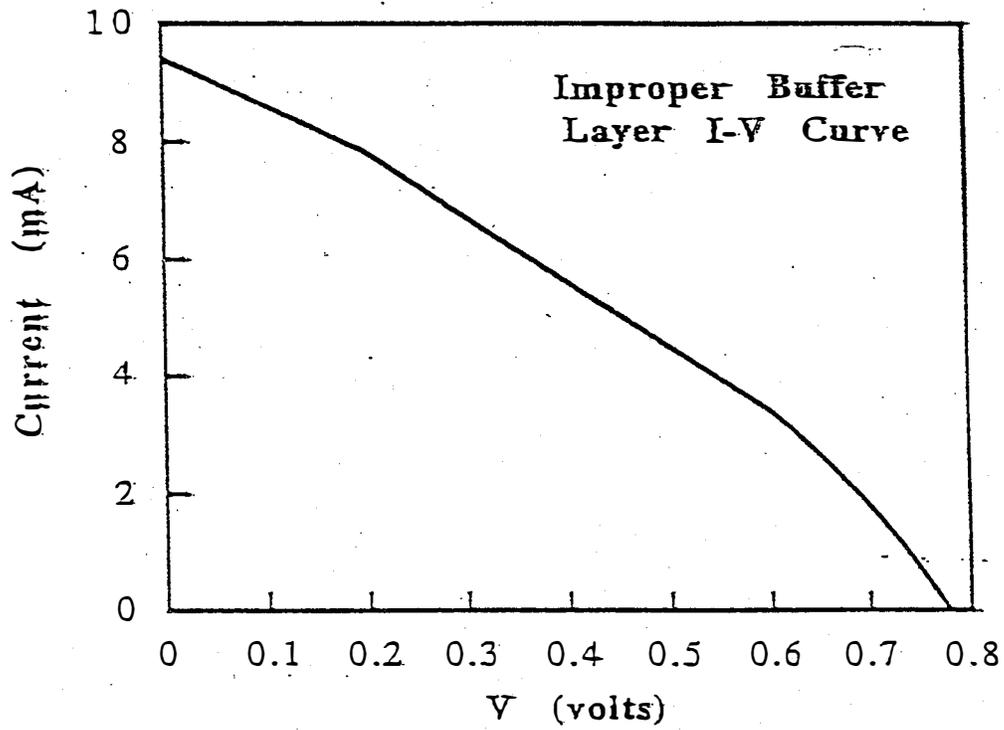


Fig. 1.4 Device with an inflexion point, caused by improper matching of valence band at p/i interface.

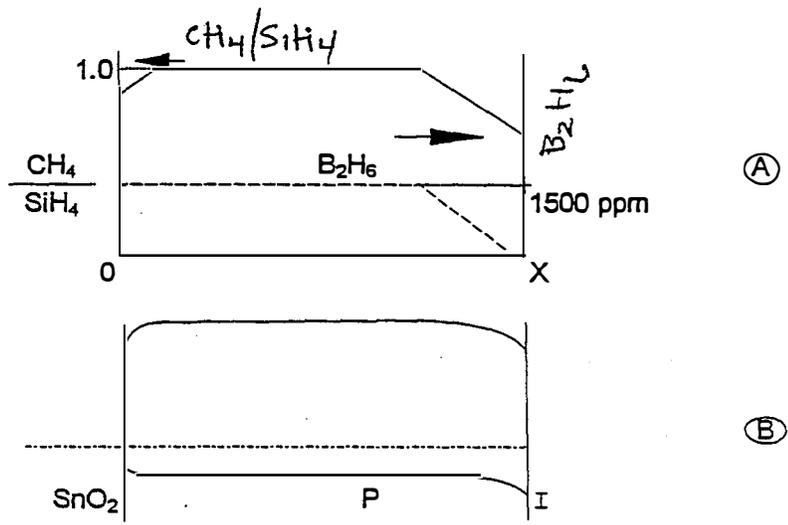


Fig. 1.5 (a) Diborane and methane grading in p layer  
 (b) Band diagram of p layer

close the shutter in front of the sample, and strike a cleaning plasma discharge to getter and bury the residual impurities. In general, the purging and plasma cleaning take about 1 hour, but succeed in removing the residual impurities. from the reactor.

After these purging and plasma cleaning procedures, a very thin (about 50 Å) a-(Si,C):H buffer layer, which is itself graded in bandgap, from a higher gap near the p layer to the a-Si:H gap near the i layer, is deposited to connect the graded p layer with the i layer. We also found that it helps to do a short (15-30 minutes) controlled diffusion of B at a higher temperature than the temperature of the succeeding i layer. In general, the fill factor is higher when we do such a diffusion, probably because the B diffuses through any thin interfacial layers, thereby smoothly connecting the p and the buffer layers. Using such careful grading of the p layer, and the buffer layer, we have been able to increase the open circuit voltage and the fill factor of the cell. Current open circuit voltages are in the range of 0.8 V, and the fill factors in the range of 0.66, all for i layers deposited at 350-370 C, using an H-ECR plasma. The i layers are deposited at growth rates of about 1.3-1.4 Å/sec, and typically are about 3500 Å thick. Thus, we have succeeded in increasing the open circuit voltage to the 0.80 V range from the previous 0.76V when deposited at these higher temperatures. (As indicated earlier, the previous 0.8V cell had been deposited at lower temperatures). We clearly need to do more work on the p layer to improve the voltage to the 0.86-0.87 V range typical of glow-discharge cells with amorphous p layers.

In Fig. 1.6, we show the I(V) curve for a typical cell, and in Fig. 1.7, we show the corresponding quantum efficiency and quantum efficiency ratio curves. Both the QE and the ratio curves were measured under a tungsten-halogen bias light of about 30 mW/cm<sup>2</sup>. Looking at the quantum efficiency curve, we find a low QE at short wavelengths, a clear indication that the p layer needs to be further optimized. In general, one would like to see blue QE at 400 nm in the range of 0.7. Looking at Fig. 1.7, the QE ratio curve is pretty flat, with a value < 1.1 across the entire range of the wavelengths. As explained earlier [1,4], such ratio curves give valuable information about the nature of carrier collection. A flat, low value (1.1 or lower) ratio curve is almost always an indication of a device with good carrier collection, i.e. a good fill factor. In contrast, if there is significant B diffusion, the ratio curve would show a high value at short wavelengths, and if there was a significant problem with hole collection, the ratio curve would give a high value for long wavelength photons. These concepts have been explained in the previous report, and in a previous paper [1,4].

### I.3 Device stability

During this year, we have started to measure the stability of devices prepared using ECR deposition techniques. At this stage, it is appropriate to ask how one should measure stability, and how one should compare the stability of a new material with the stability of standard glow-discharge deposited cells. These are not trivial questions, especially since, in new materials, not all parameters are as optimized as in the glow discharge cells. It is important that we address the physics of stability, and see what it tells us about how to compare stability of cells.

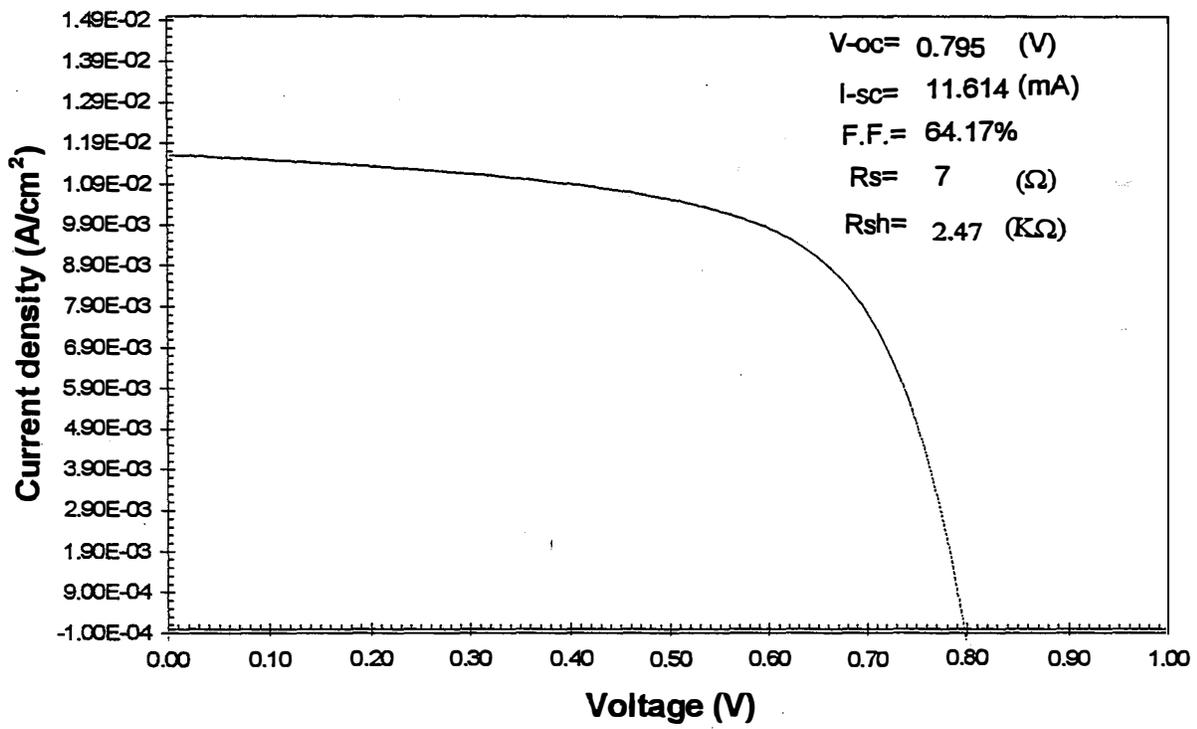


Fig. 1.6 Device I(V) curve for a good device

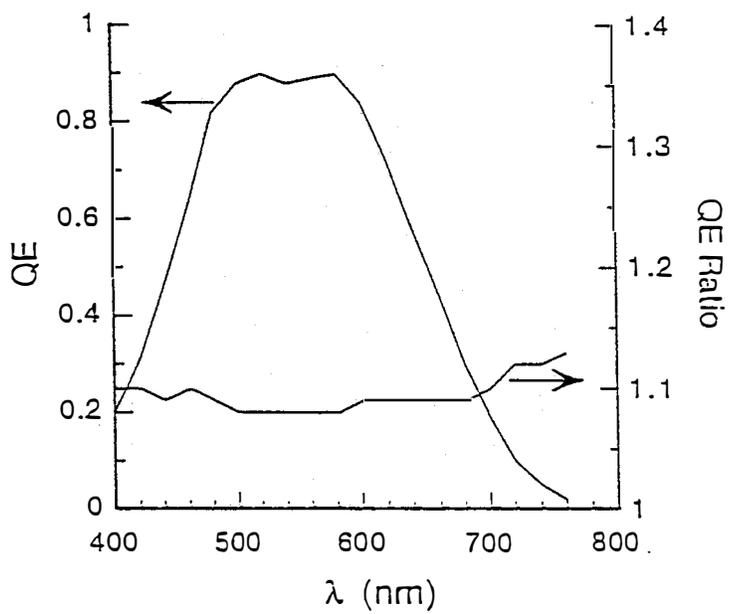


Fig.1.7 QE and Quantum efficiency ratio[ QE( 0 V)/ QE(+0.4V)] for device of Fig. 1.6.

The first point to remember is that if we are trying to compare the stability of a new material-i layer in a cell with the stability of i material in a glow-discharge cell, the two cells must have comparable thicknesses of the i layer. Only then can one compare measurements such as quantum efficiency and quantum efficiency ratios, which give us valuable insights into hole mobility-lifetime products and electric field profiles.

The second point to remember is that since we are trying to see if a new material is better than the glow-discharge material in terms of stability, it is essential that the fill factors of solar cells be comparable in both cases. It makes little sense to compare a cell with 40% fill factor with one with 70%. The 40% FF cell may be more stable, but is the material in it any good? If the material is initially dead, it remains dead.

The third point is that to study realistic degradation, the amount of light reaching the layers of the cells must be comparable for both cells. In particular, this means that using Schottky barriers to measure stability of new material-cells is dangerous, and may give rise to meaningless results, because light transmission through Schottky barriers is notoriously variable from one cell to the next. It is only when green and red external quantum efficiencies are comparable in the two cells that one can be reasonably sure that approximately the same number of photons are reaching the i layer in each case, and therefore, the recombination traffic is similar in each case. With Schottky barriers, it may be more appropriate to use a light intensity that gives the same current as would have been obtained in a p-i-n cell with the same i layer.

The fourth point to note is that while interface recombination is not generally a major factor in causing the instability in normal glow-discharge cells, this assumption must be carefully tested for each new material. As an example, for a-(Si,C):H i-layer cells, this assumption may not be valid. Also, it may not be valid for a-(Si,Ge):H cells.

The fifth point to make is that the open circuit voltage of cells being compared should be similar, because  $V_{oc}$  gives an indication of the built-in voltage in the cell. There is no point in comparing a cell with a higher voltage( hence, built-in field) with one having a significantly lower voltage( and hence, lower E field.)

In this sense, there is some caution to be used when comparing p-i-n cells with Schottky cells, because of the much lower voltages in the Schottky barrier cells.

The final point to note is that the spectrum of the illumination may matter, especially if the interfacial instability is important in a given cell. In particular, having a blue-poor spectrum for light soaking lamp may give a false reading for certain kinds of cells, though not necessarily for midgap alloy cells, i.e. cells which are going to be the second cell in a tandem structure.

Having made these points, we describe below the results of light soaking tests performed on two nearly identical cells, one prepared using standard triode glow-discharge deposition, and one using ECR deposition. We tried to keep the two cells comparable, by having the same voltages,

fill factors and quantum efficiencies. Since the ECR cell generally had a lower voltage(0.76 V) compared to the normal glow-discharge cell(0.84-0.9), we deliberately prepared glow discharge cells with lower voltages(0.76 V) by altering the p layer of the cell. We also tried to match the red quantum efficiencies of the two cells, by keeping the thicknesses of the i layers the same in each cell. Each cell had similar Tauc-gaps ( 1.75 eV).

In Fig. 1.8 and 1.9, we show the initial I(V) curves of the two cells, and in Fig. 1.10 and 1.11, the quantum efficiencies and the quantum efficiency ratios. It is clear from this comparison that the two cells are very similar. Each cell has a good fill factor, about 0.67. Each cell had an Al back contact. Note that our glow discharge cells was without H dilution, and may not represent the best, most stable glow discharge cell of today. Comparisons with such H-diluted cells obtained from Solarex are in progress.

$$J_{sc} = 11.2 \text{ mA/cm}^2$$

$$V_{oc} = 0.76 \text{ V}$$

$$F = 0.665$$

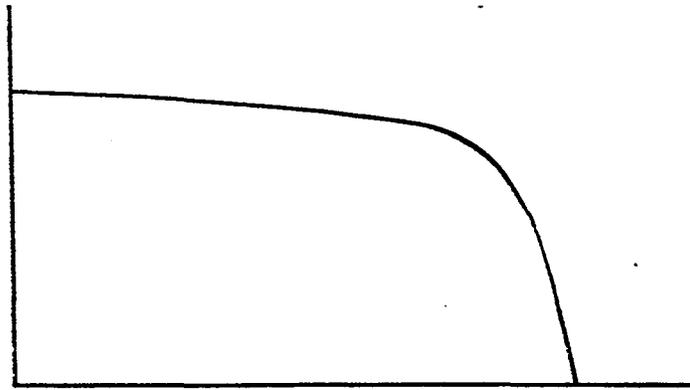


Fig. 1.8 Initial I(V) curve of ECR cell selected for stability measurements

$$J_{sc} = 13.1 \text{ mA/cm}^2$$

$$V_{oc} = 0.76 \text{ V}$$

$$F = 0.67$$

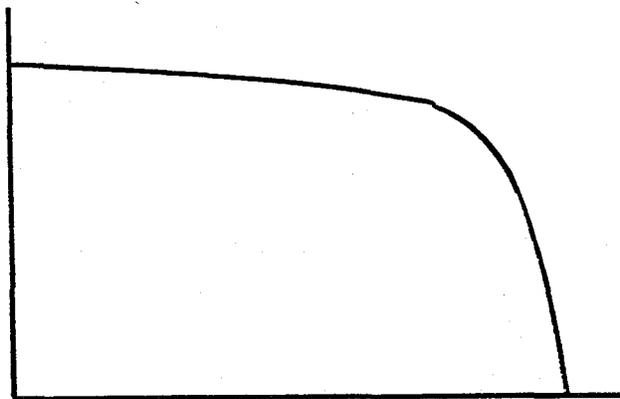
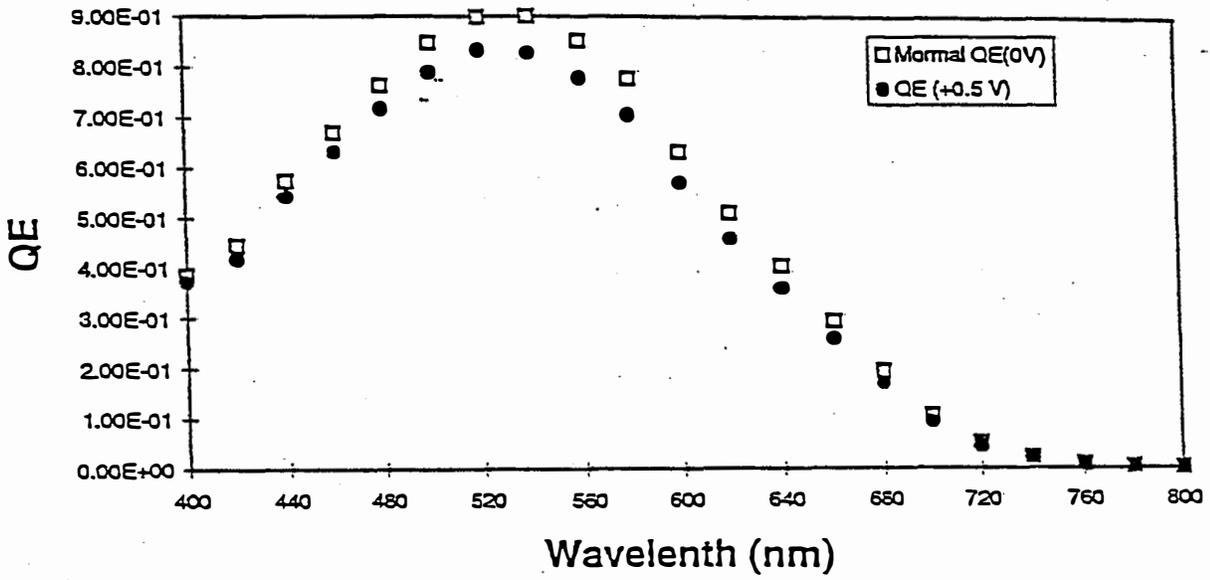


Fig. 1.9 Initial I(V) curve of glow-discharge cell selected for stability measurements

2/1365



2/1365

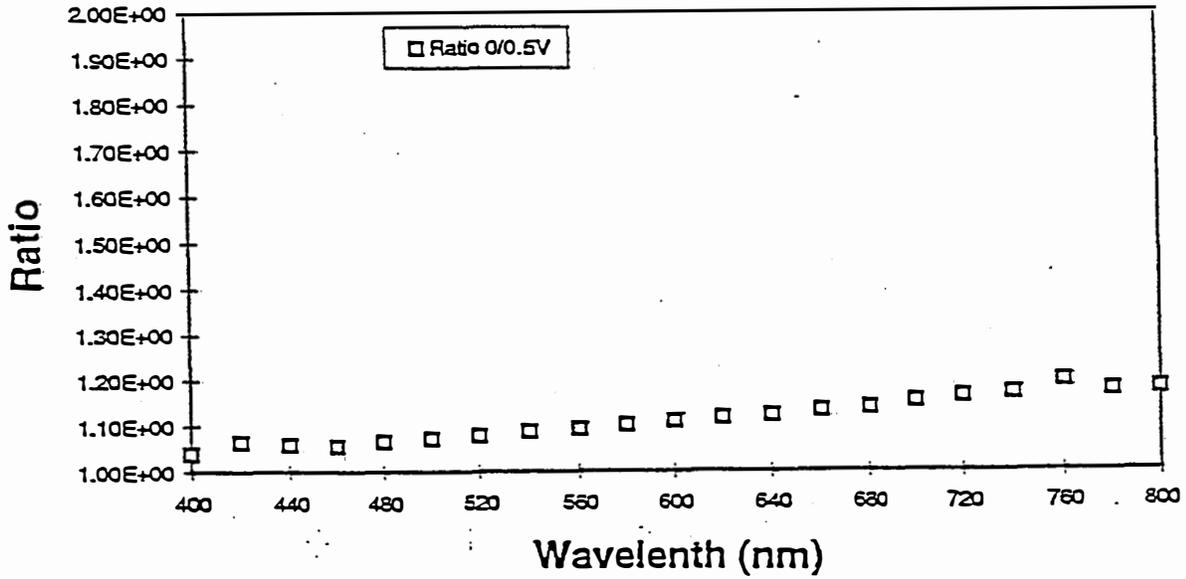


Fig. 1.10 QE and QE ratio curves for the ECR cell(initial)

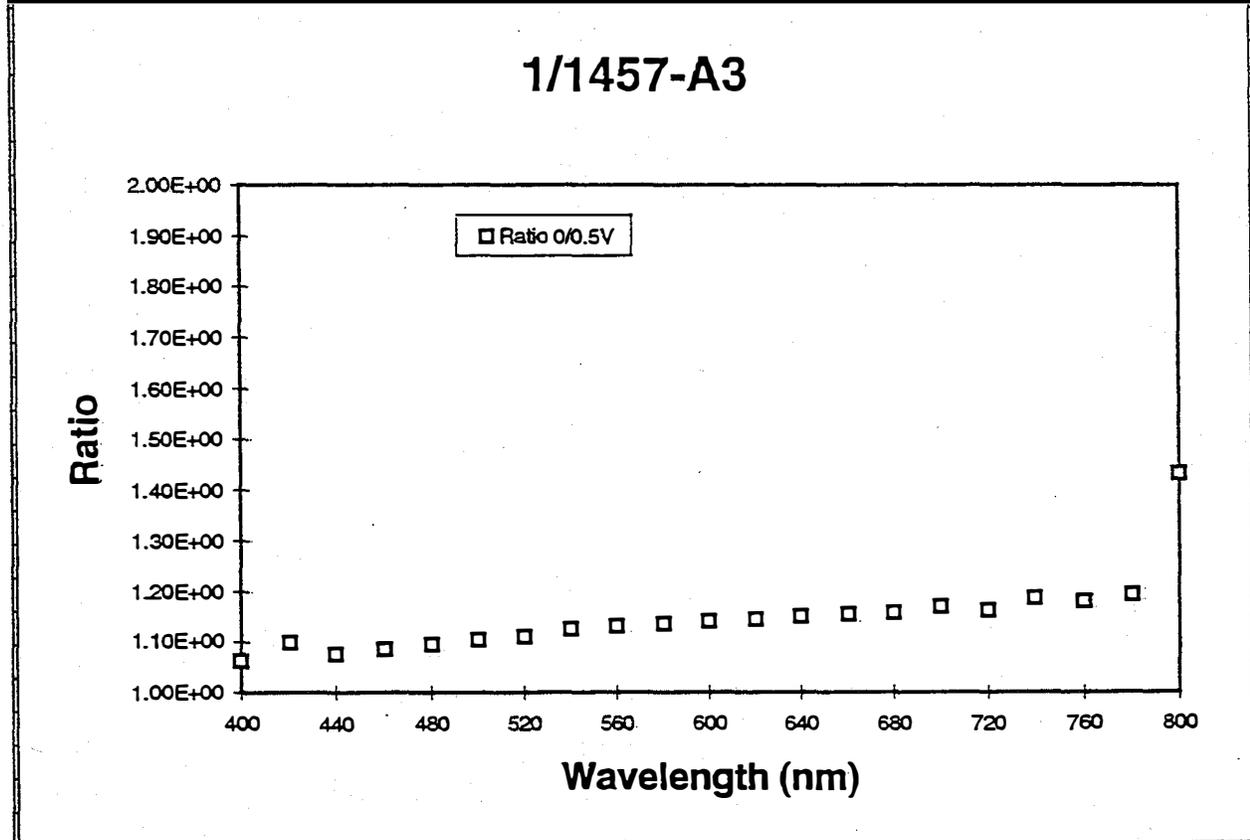
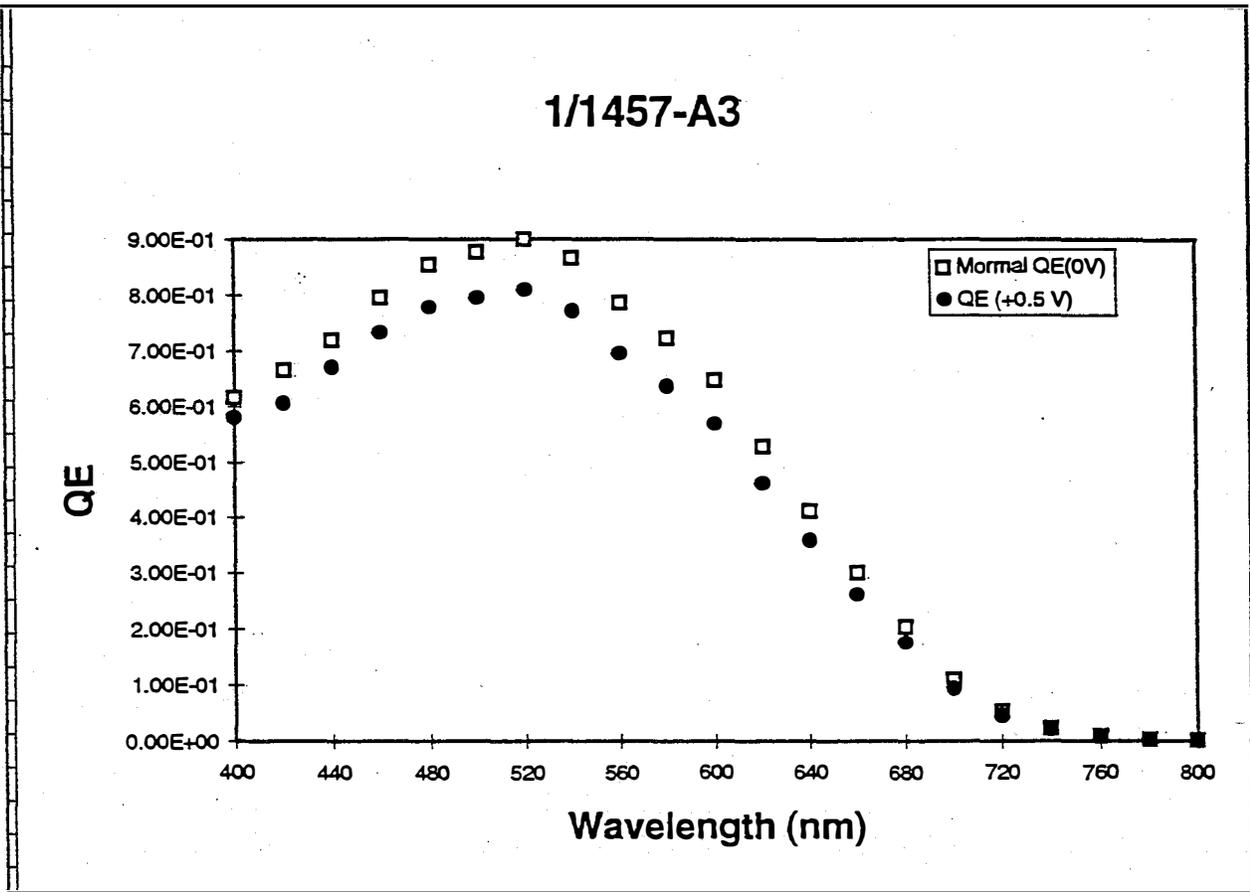


Fig. 1.11 QE and QE ratio curves for the glow discharge cell(initial values)

The two cells were light soaked using ELH lamp at 300 mW/cm<sup>2</sup> intensity. The changes in the parameters of the cells after light soaking are shown in Table 1.1. In Fig. 1.12, we show the relative degradation in current, voltage and fill factor for each of the cells. From the table, it appears that the cell produced using ECR deposition is much more stable than the glow-discharge produced cell. In Fig. 1.13, we show the quantum efficiency ratio( ratio of QE at 0V to the QE at +0.4 V) for each of the two cells after degradation. It is clear from Fig. 1.13 that the ratio for the glow-discharge cell is much higher than for the ECR cell, a clear indication that the holes in the glow-discharge cell need a greater field assist for collection. This fact suggests that the hole mobility-lifetime product has degraded more in the glow-discharge cell than in the ECR cell. This, in turn means that the i material in the ECR cell has degraded less than the i material in the glow-discharge cell. Thus, we have an experimental proof that indeed, the ECR material is more stable than the non-Hydrogen diluted glow-discharge material, even when incorporated in a cell.

This is a very satisfying result, because it shows that new materials can indeed lead to better stability in cells. The result is also satisfying because it confirms the results on studies of materials done earlier,[1], suggesting that careful studies of material properties in films indeed lead to conclusions that can be valid even when the material is incorporated in devices. We clearly need to do more work on other ECR cells, with higher voltage, and compare those cells with H-diluted glow discharge cells which are more representative of the state-of-the-art in glow discharge. We plan to do such experiments in the future.

Table 1.1  
Comparison of degradation of ECR and glow-discharge cells

		$J_{sc}$ (mA/cm <sup>2</sup> ) (V)	$V_{oc}$	FF
GD	Annealed	13.1	0.76	0.67
	Degraded	11.8	0.725	0.53
ECR	Annealed	11.2	0.76	0.665
	Degraded	10.5	0.765	0.605

Much more work needs to be done on this material system. In particular, we need to make devices using i layers with the sub-ppm Boron compensation that we described earlier[2]. We had shown that such material is the most stable and the least defective of any material we had examined. We also need to work on improving the voltages to the 0.86 V level, which would make the devices comparable to most glow-discharge devices. Finally, we need to develop the highly reflecting back contact(ITO/Ag) so that we can obtain a 20% increase in current. These tasks will all be addressed during the next year.

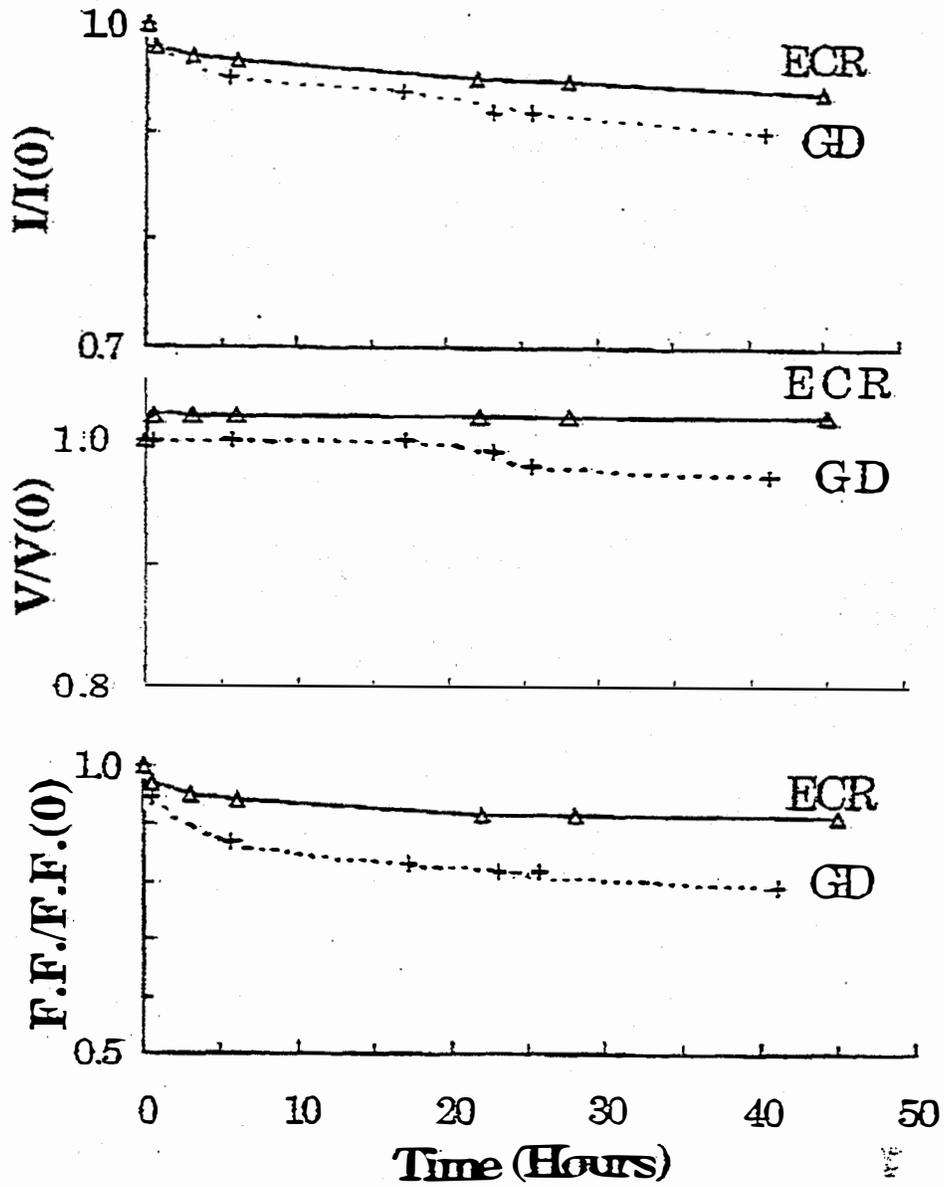


Fig. 1.12 Changes in current, voltage and fill factor of ECR and glow-discharge cells as functions of light soaking time. 3 x sun illumination, ELH lamp.

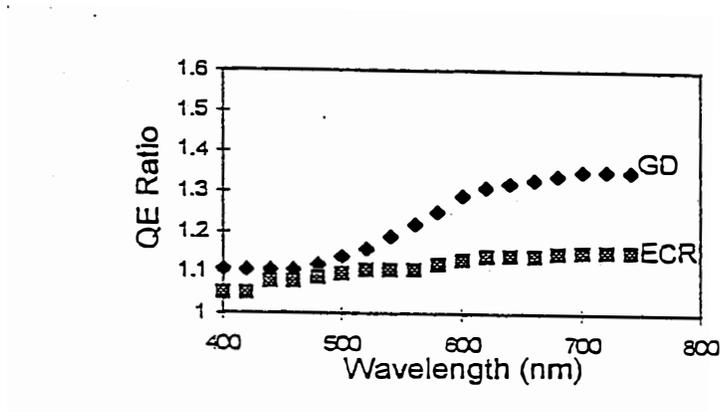


Fig. 1.13 QE ratio for glow-discharge and ECR cells after degradation.

## Chapter II

### Research on Amorphous Silicon-Germanium Materials

#### II.1 Introduction

In the final report for the previous contract,[1], we reported on the measurements of electronic properties of a-(Si,Ge):H films and devices made using RF triode glow-discharge deposition. There, we showed that the properties such as electron and hole  $\mu\tau$  products degraded with increasing Ge content, and Urbach energies for valence band tails, and subgap absorption  $\alpha$  at the shoulder increased with increasing Ge content. In this report, we examine the electronic properties of films deposited using remote, low pressure ECR plasma discharge.

#### II.2 Deposition conditions

The deposition apparatus is similar to the one described in Chapter I( See Fig. 1.1 ). A beam of energetic He or H ions, created by the ECR discharge, travels towards the substrate and reacts with a mixture of silane and germane, introduced near the substrate, to produce a-(Si,Ge):H films. The feedstock gases are pure silane, and germane diluted 10% in hydrogen. The substrate is heated externally, and the reactor is capable of in-situ plasma gettering, using a shutter in front of the substrate, and typically pumps down to about  $3 \times 10^{-8}$  T after outgassing. A virtual load-lock arrangement is used to load and unload substrates. In this arrangement, a cap, which is identical to the substrate holder, is used to assist in transfer of the substrate from and into the reactor. The transfer process takes about 5-7 seconds, and during the transfer, the reactor is flushed with nitrogen. This way, moisture contamination of the reactor is avoided, and the reactor pumps down very rapidly.

The typical deposition conditions are listed in Table I below:

Table I

#### Range of Deposition conditions

Silane flow	: 2-4 sccm
10% Germane/hydrogen flow	: 3-6 sccm
Helium flow	: 45 sccm
Hydrogen flow	: 40 sccm
Substrate temperature	: 300-375 C
Microwave power	: 40-130 W
Growth rate of films	: 1-1.5 A/sec
Pressure	: 10-25 mT

#### II.3 Plasma properties

Since plasma discharge for He is very different from the plasma discharge for H, we measured the properties of H and He ECR-plasma discharges near the substrate using Langmuir probes[5]. In Fig. 2.1-2.6, we present the results of the Langmuir probe measurements of the ion current, electron temperatures, and plasma potentials as functions of pressure for a He and a H discharge. From these figures, we can conclude that the He discharge, in general, produces a higher energy plasma than a comparable H discharge. As an example, at 10 mT pressure, a He discharge of 100 W microwave power has plasma potential of 15 V, whereas a comparable H<sub>2</sub> discharge has a potential of only 8 V. The combination of a higher ion potential, and a higher ion mass when using He as compared to using H, leads to significantly more energetic ion bombardment of the film when using He as the discharge gas. This fact may have some bearing on the results that we will report in the following sections.

## II.4 Electronic properties

The properties measured were:

H content by FTIR measurements

Ge concentration in films by EDAX

Dark conductivity

AM1.5 Photoconductivity

Subgap absorption by two-beam photoconductivity

Urbach energy from subgap absorption

Optical absorption using spectrophotometer

### *1. H concentration*

A typical IR spectrum for a film is shown in Fig. 2.7. From such measurements, we can estimate the bonded H concentration, which is shown in Fig. 2.8 as a function of Tauc gap, for films made using either He and H<sub>2</sub> as the plasma gas. The difference in H concentrations between the two films is striking. The very low values of H concentration for films made using He dilution is particularly noteworthy, and translates into a lower gap for a-Si:H made using He as compared with H. Note that the H concentration is lower than normally reported in the literature.[1]. We do not see any significant SiH<sub>2</sub>-type bonding in these films, unlike results reported previously in the literature[1].

### *2. Ge content*

We have measured Ge content using energy dispersive analysis(EDAX).In Fig. 2.9, we show Tauc gap as a function of Ge content for films made using either H<sub>2</sub> or He as the plasma gas. We notice that the Tauc gaps for films made using He as the plasma gas are much lower than for films made using H<sub>2</sub> as the plasma gas. This means that to get a given bandgap, we use less Ge when using He than when using H<sub>2</sub>. Typically, for the same Ge content, we obtain a Tauc gap which is lower by 60 meV when using He as the plasma gas as compared to using H<sub>2</sub>.

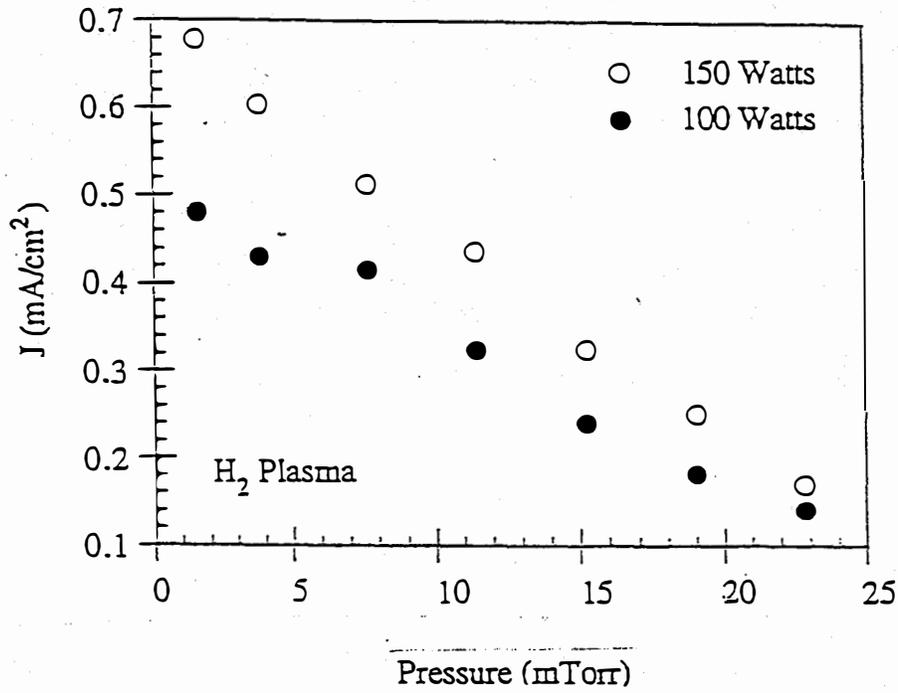


Fig.2.1 Variation in ion current as a function of chamber pressure in Hydrogen-ECR plasma

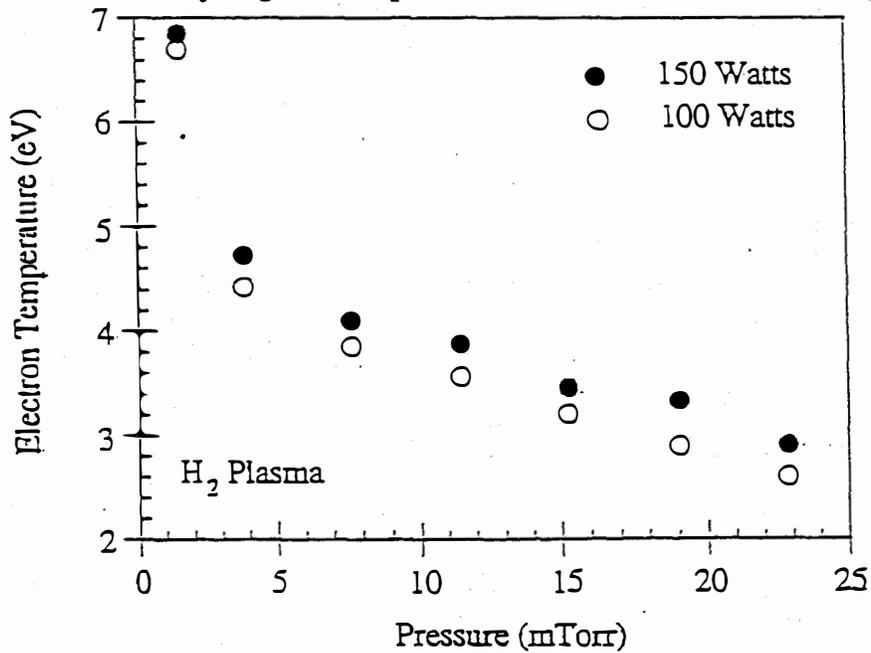


Fig. 2.2 Variation in electron temperature as a function of pressure in H-ECR plasma

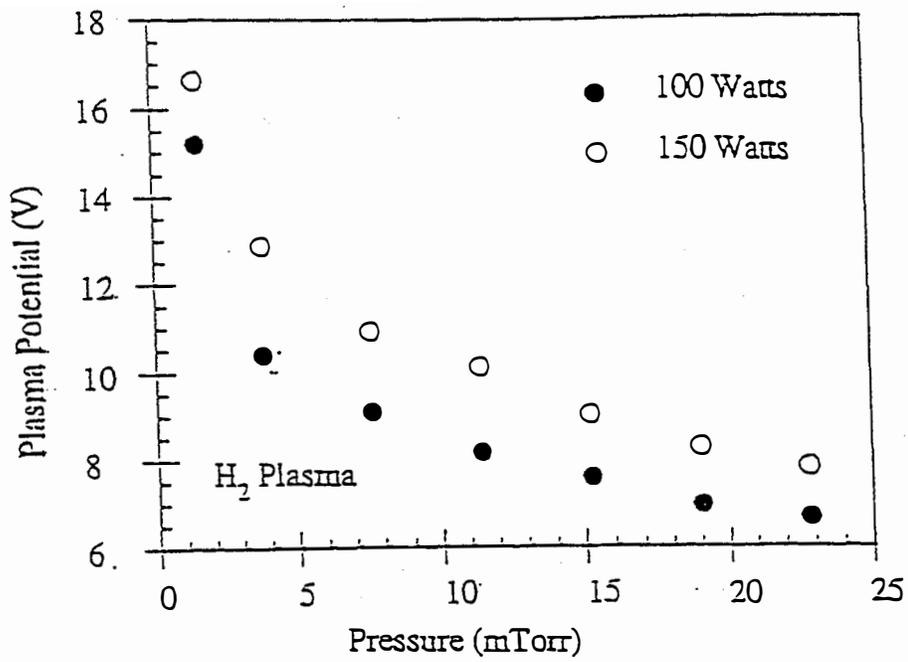


Fig. 2.3 Variation of the plasma potential with chamber pressure.

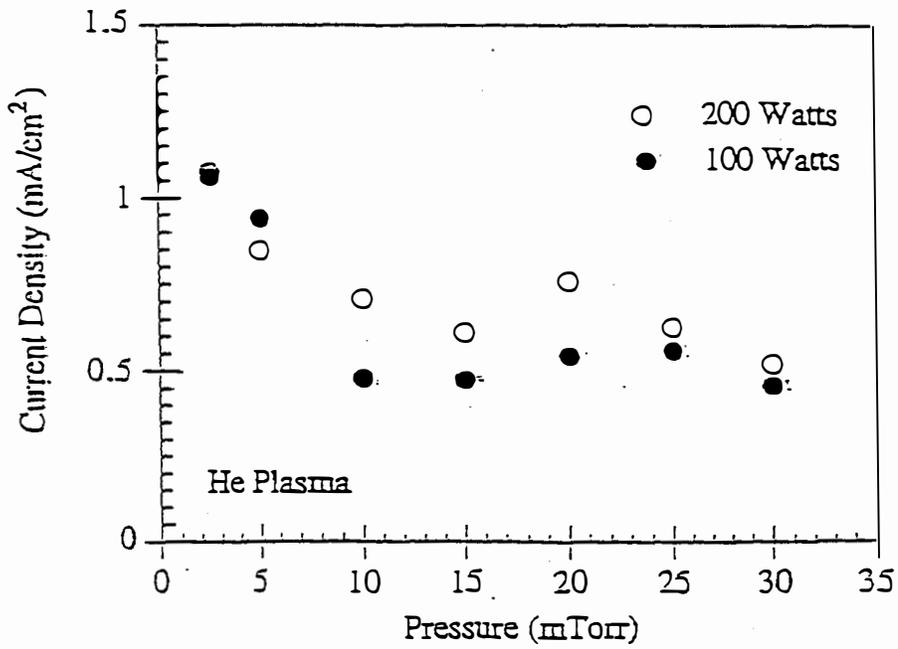


Fig. 2.4 Variation of the current density with pressure in a helium plasma.

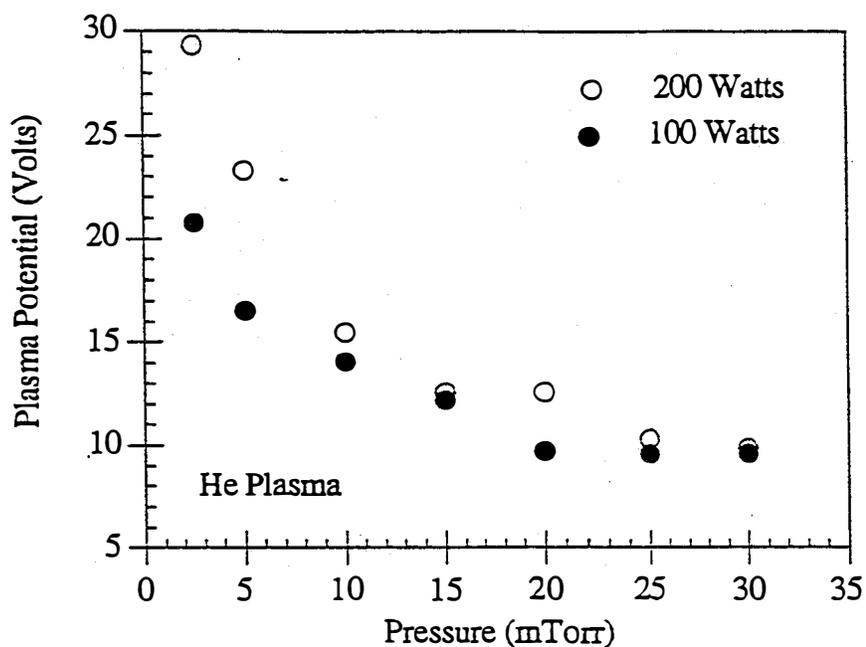


Fig. 2.6 Variation of the plasma potential with pressure in a helium plasma.

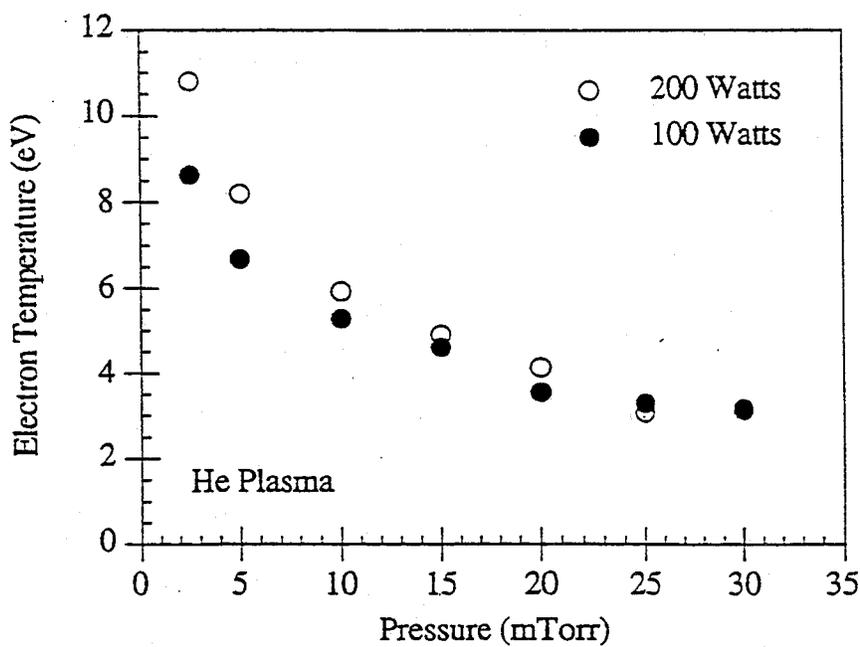


Fig. 2.5 Variation of the electron temperature with pressure in a helium plasma.

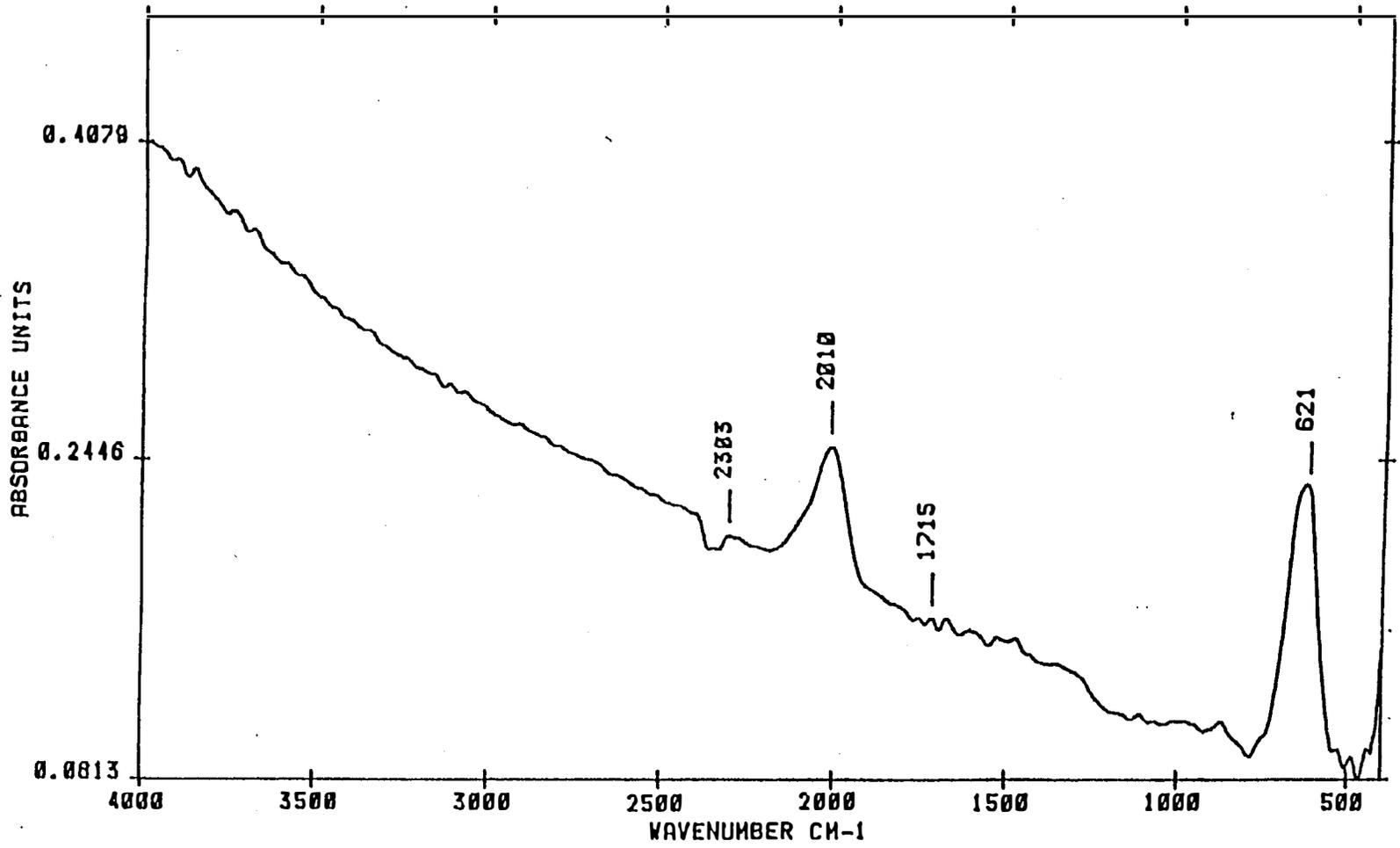


Fig. 2.7 The IR absorption spectra of sample 2/1548.

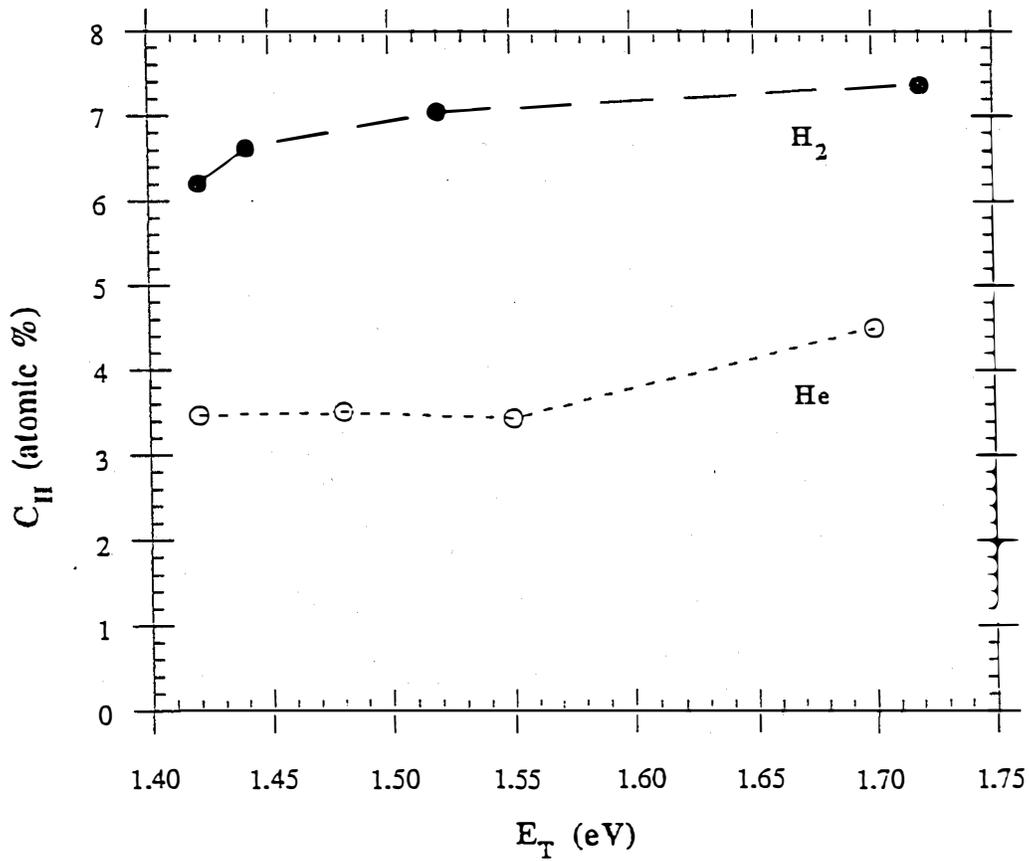


Fig. 2.8 Bonded H concentration in a-(Si,Ge):H films as a function of Tauc gap for films deposited using either  $H_2$  or He dilution

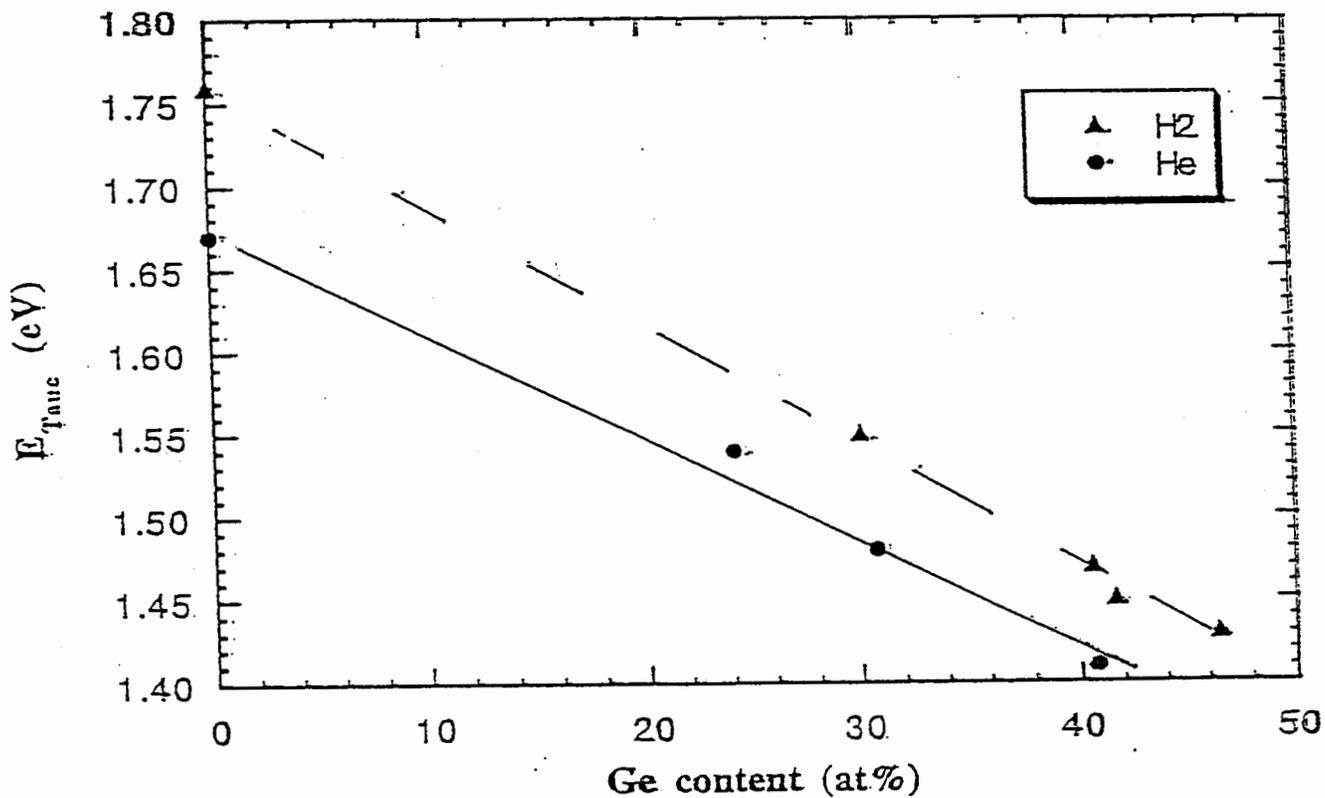


Fig. 2.9 Tauc gap of a-(Si,Ge):H films as a function of Ge concentration for ECR-deposited films using either He or H<sub>2</sub> as the diluent gas

### ***2.4.3 Dark and Photo-conductivities***

In Fig. 2.10, we show the photo-conductivity of a-(Si,Ge):H films made using H or He dilution as a function of Tauc bandgap. In Fig. 2.11, we plot the corresponding dark conductivities, and in Fig. 2.12, the photo-sensitivities(photo/dark conductivity) for both H and He films. From these figures, we conclude that the use of He as the plasma gas seems to lead to lower dark conductivities(Fermi levels further down in the gap), and higher photo-sensitivities than the use of H as the plasma gas. Please note that the photo-sensitivities with the He discharge are the best ever reported over the Tauc bandgap range of the alloys studied[4]. Therefore, we are currently focussing on these low H content films as potential device grade materials.

#### **4. Subgap absorption and Urbach energy for valence band tails**

These were measured using two-beam photoconductivity techniques[2]. The results for a typical film of 1.54 eV Tauc gap made using He are shown in Fig. 2.13, showing a low value of both subgap  $\alpha$  and Urbach energy. In Fig. 2.14 we show the relationship between subgap  $\alpha$  and Tauc gap for films made using He as the plasma gas, and in Fig. 2.15, the relationship between Urbach energy  $E_{ov}$  and Tauc gap for the same films. In both figures, we compare the values obtained in our He-ECR films with the values obtained in glow-discharge films deposited using H<sub>2</sub>-dilution that we reported in our earlier report.[3]. Note that, previously, when we had used He dilution for glow-discharge deposition of a-(Si,Ge):H, the results were worse than with H<sub>2</sub> dilution. From figures 2.14 and 2.15, it is clear that the films deposited using He-ECR discharge appear to be of higher quality( lower subgap  $\alpha$ , lower Urbach energy ) than films made using glow-discharge deposition. This is an encouraging result, and we plan to incorporate these films into devices during the next year. The work on H<sub>2</sub>-diluted ECR films is not yet complete, and we need more data before we can assess the quality of those films.

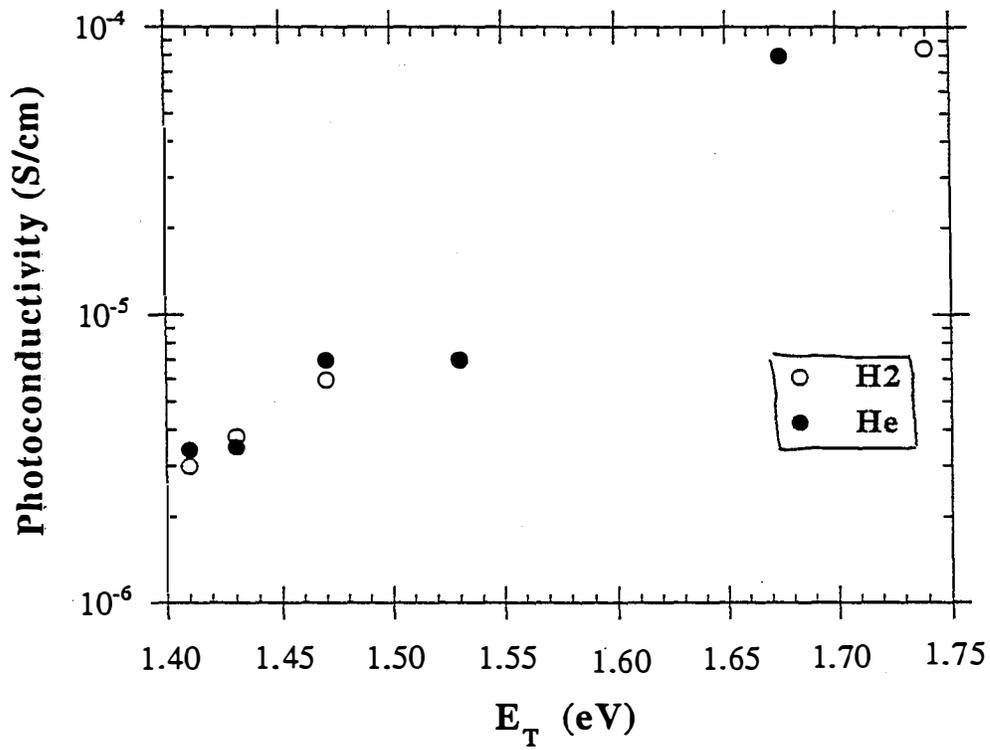


Fig. 2.10 Photo-conductivity of a-(Si,Ge):H films as a function of Tauc gap using either He or H<sub>2</sub> as the diluent gas

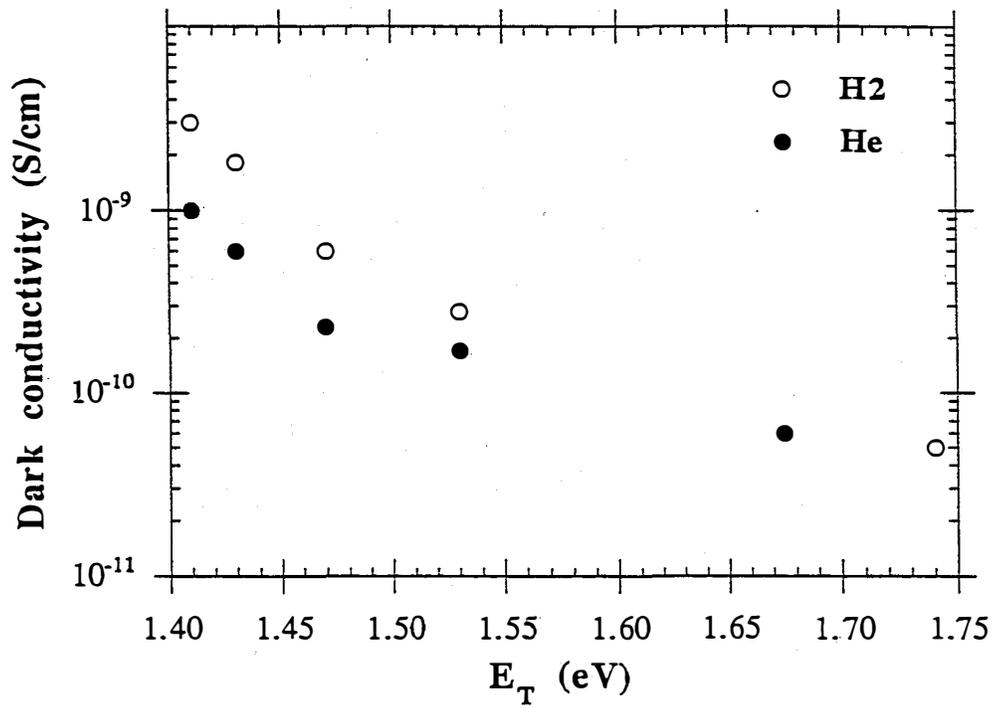


Fig.2.11 Dark conductivity of a-(Si,Ge):H films, deposited using either He or H<sub>2</sub> as the diluent gas

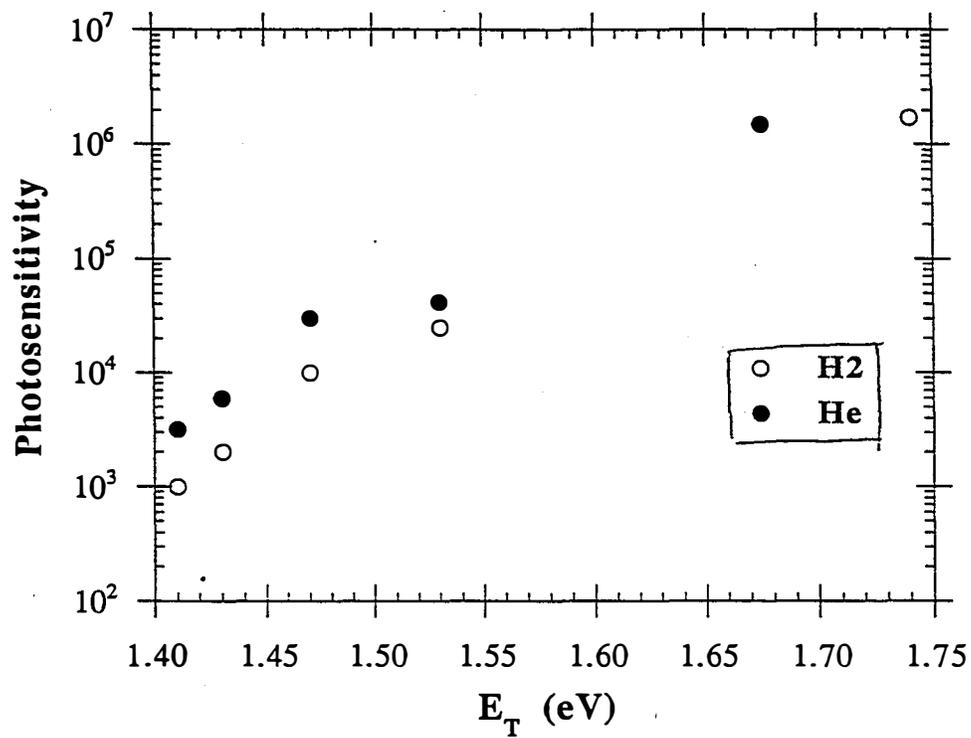


Fig. 2.12 Photo-sensitivity of a-(Si,Ge):H films, deposited using either He or H<sub>2</sub> as the diluent gas

Absorption Data for a-(Si,Ge):H film of 1.54 eV

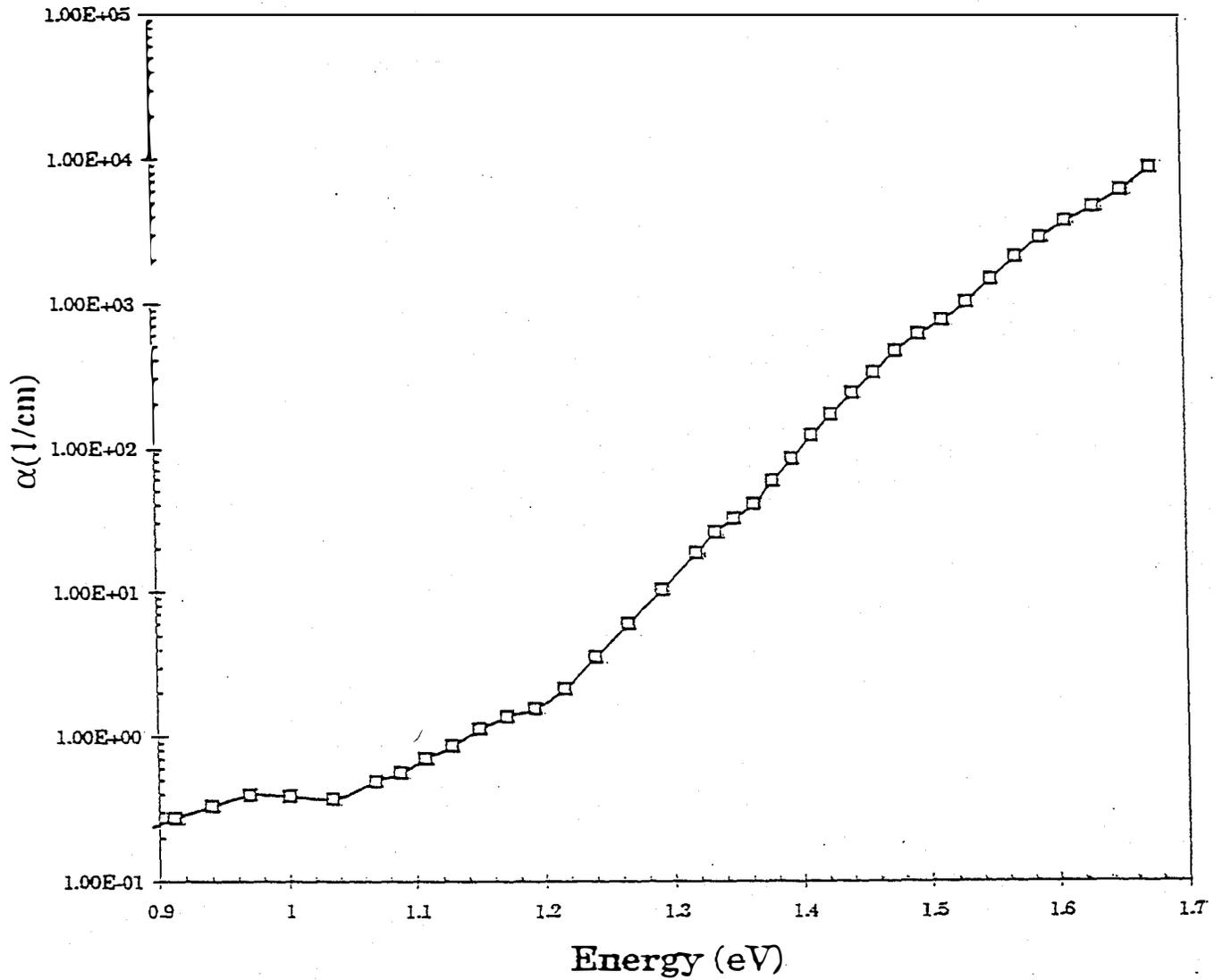


Fig. 2.13 Subgap absorption of a-(Si,Ge):H film

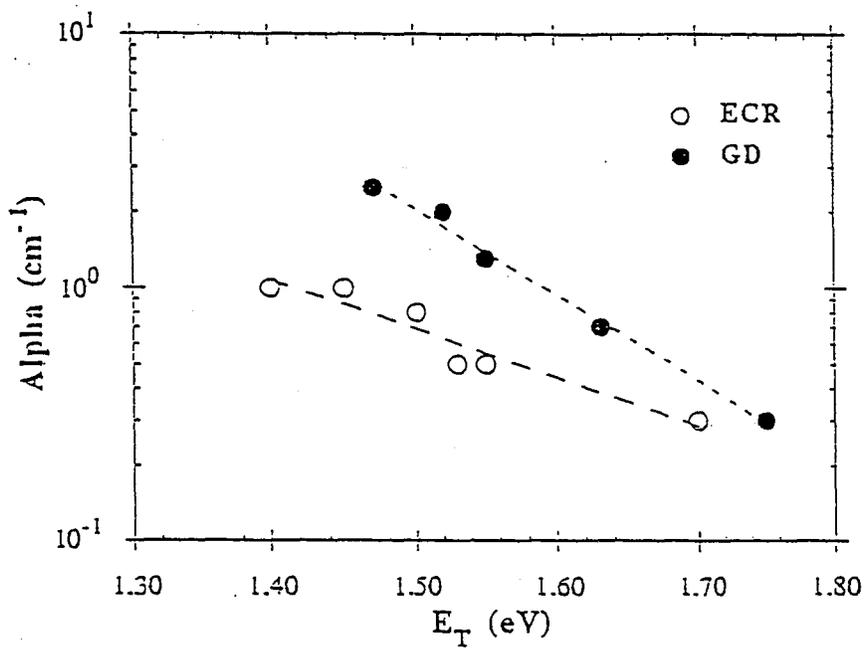


Fig. 2.14 Subgap  $\alpha$ , measured at the shoulder, vs. Tauc gap for a-(Si,Ge):H films deposited using two techniques

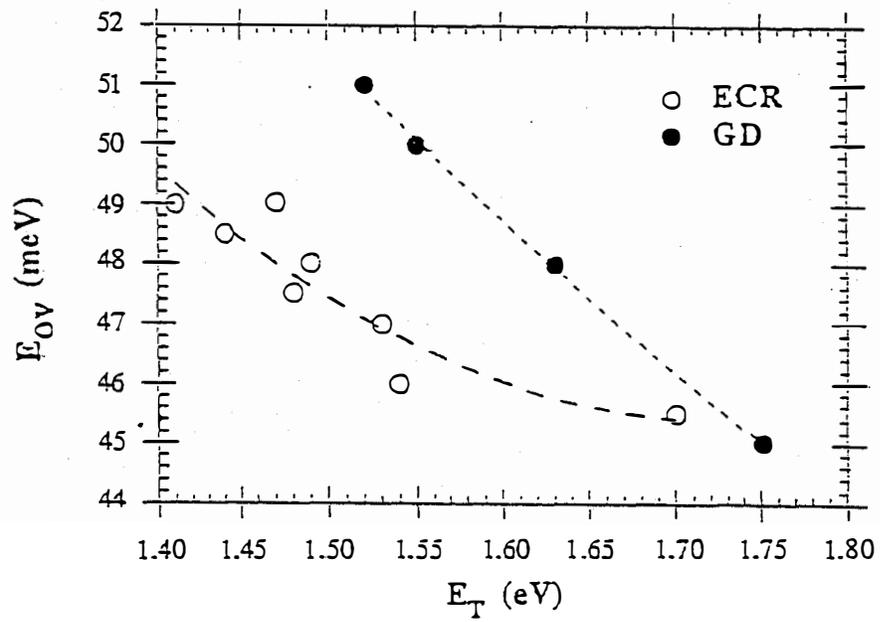


Fig. 2.15 Urbach energy vs. Tauc gap for a-(Si,Ge):H films deposited using either glow discharge or ECR technique

## II.5 Discussion

We have shown that the films made using He as the discharge gas generally have a lower H concentration than a film of the same bandgap made using H as the discharge gas. We speculate that this lower H concentration, and a correspondingly lower bandgap for any Ge concentration in the film, is a result of the intense ion bombardment of the film under a He discharge. It is also possible that since He does not chemically react with Si or Ge, it is not leading to an etching of the film as it grows. Such etching is known to increase the bandgap[6], and the absence of etching may also contribute to a lower gap when using He as compared to using H as the discharge gas.

The interesting properties of the films produced using He as the discharge gas lead to many possibilities for device design. It appears that bandgap grading in devices can be achieved simply by exchanging H and He during the growth process, thereby offering yet another way of achieving grading of the i layer. The low values of H in these films ought to lead to better stability, an experiment that we plan to do.

## II.6 Summary of Research on a-(Si,Ge):H films

In summary, we have studied the electronic properties of a-(Si,Ge):H films deposited using ECR low pressure deposition process. The properties of the film depend upon the deposition conditions, particularly upon whether H<sub>2</sub> or He is used as the plasma gas. When the films are deposited with He as the plasma gas, the H content of the films is significantly less than when they are deposited with H<sub>2</sub> as the plasma gas. Also, the Tauc gap of the films deposited with He is lower than the Tauc gap of films deposited with H<sub>2</sub>, for the same Ge content in the film. Even for straight a-Si:H, we obtain a lower Tauc gap (1.67 eV) with He-ECR than the film deposited with H-ECR (Tauc gap of 1.75 eV). The films deposited using He appear to have superior electronic properties than either glow-discharge, or H-ECR films. Future work will concentrate on making devices in these films, and on investigating stability properties in these films.

## References

1. V. L. Dalal, Final report under NREL subcontract XAN-4-10063-8
2. V. L. Dalal, E. Ping, M. Bhan, S. Kaushal and M. Leonard, Appl. Physics Lett., 64,1862(1994)
3. J. H. Thomas and A. Catalano, Appl. Phys. Lett. 43,101(1983)
4. R. Knox, V. L. dalal and O. Popov, J. Vac. Sci. Tech. A9, 474(1991)
5. V. L. Dalal, M. Leonard, J. Booker and A. Vaseashta, Proc. of 18th. IEEE Photovolt. Conf.,p.523(1985)
6. V. L. Dalal, C. M. Fortmann and E. Eser, Proc. of AIP Conference, Vol. 73,31(1981)

# REPORT DOCUMENTATION PAGE

*Form Approved*  
OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 1996	3. REPORT TYPE AND DATES COVERED Annual Technical Report, 31 May 1994 - 30 May 1995.	
4. TITLE AND SUBTITLE  Comprehensive Research on Stability and Performance of a-Si:H and Alloys; Phase I Team Annual Technical Report, 31 May 1994 - 30 May 1995		5. FUNDING NUMBERS  C: XAN-4-13318-08 TA: PV631101	
6. AUTHOR(S)  Vikram Dalal		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Iowa State University Ames, Iowa			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393		10. SPONSORING/MONITORING AGENCY REPORT NUMBER  TP-451-21601  DE96013078	
11. SUPPLEMENTARY NOTES  NREL Technical Monitor: B. von Roedern			
12a. DISTRIBUTION/AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE  UC-1262	
13. ABSTRACT ( <i>Maximum 200 words</i> )  This report covers the research done during the first phase of the subcontract. During this period, we concentrated on two areas: improving the voltage and stability of a-Si:H devices made using electron cyclotron resonance (ECR) deposition, and improving the properties of a-(Si,Ge):H films, also using ECR deposition. In the area of device research, we successfully solved the difficult problem of controlling B diffusion at high temperatures from p into i layers in superstrate devices (where the p layer is the first layer deposited on a transparent conducting oxide). In our ECR technique research we systematically studied the deposition of a-(Si,Ge):H films using remote, low-pressure ECR techniques. We used two gases, H <sub>2</sub> and He, as the primary plasma-region gases, and we found that the properties of the film depend on which gas is used as the plasma gas. We find that the plasma potentials and ion energies are higher for He than for H <sub>2</sub> plasma conditions. We believe that significant ion bombardment when He is used may account for the lower H content and the better electronic properties.			
14. SUBJECT TERMS  photovoltaics ; amorphous silicon alloys ; electron cyclotron resonance ; ECR deposition		15. NUMBER OF PAGES 45	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL