PRODUCTION AND EVALUATION OF a-GaAs SOLAR CELLS

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
FEBRUARY 1, 1980 - APRIL 30, 1980

William Paul, Principal Investigator
Dilip K. Paul, Staff Scientist

June 1980

DISCLAIMER

This book 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.

Work Performed Under Contract DE-AC03-79ET23036

HARVARD UNIVERSITY
DIVISION OF APPLIED SCIENCES
CAMBRIDGE, MASSACHUSETTS 02138

MASTER

DISCLAIMER

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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

PRODUCTION AND EVALUATION OF a-GaAs SOLAR CELLS

QUARTERLY TECHNICAL PROGRESS REPORT
FOR PERIOD FEBRUARY 1, 1980 - APRIL 30, 1980

WILLIAM PAUL
Principal Investigator

DILIP K. PAUL
Staff Scientist

JUNE 1980

HARVARD UNIVERSITY
DIVISION OF APPLIED SCIENCES
CAMBRIDGE, MASSACHUSETTS 02138

PREPARED FOR THE
U.S. DEPARTMENT OF ENERGY
SOLAR ENERGY
UNDER CONTRACT DE-AC03-79ET23036

ABSTRACT

Hydrogenated alloys of a-GaAs have been prepared by r.f. sputtering in a mixture of argon and hydrogen at several partial pressures, substrate temperatures and r.f. powers. We report the results of a systematic investigation of the microstructural properties of these films by SEM and TEM, and attempt its correlation with the deposition parameters and other electronic properties.

DESCRIPTION OF PROJECT

The purpose of this project is i) to produce and dope a-GaAs alloys, principally with hydrogen, and ii) to evaluate their potential for low-cost solar cell material.

The approach adopted was to r.f. sputter GaAs in the presence of hydrogen or dopant gases such as PH_3 and B_2H_6 , and to vary the conditions of preparation such as substrate temperature, hydrogen partial pressure, argon sputtering gas pressure, sputtering rate and r.f. power. Subsequently, the films were to be characterized with regard to their chemical, structural, electronic and optical properties, and a model for the band structure, defect structure, transport and recombination properties was to be sought from these measurements. Evaluation of device potential was to be activated at an appropriate time after the films show promising properties as judged by the characterization schemes.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
ABSTRACT	i
DESCRIPTION OF PROJECT	ii
INTRODUCTION	1
PREPARATION OF FILMS & MICROSTRUCTURAL CHARACTERIZATION . . .	1
CORRELATION OF MICROSTRUCTURE WITH DEPOSITION PARAMETERS & ASSOCIATED PROPERTIES OF FILMS	2
CONCLUSIONS AND FUTURE PLANS	20
REFERENCES	21
DISTRIBUTION LIST	22

LIST OF FIGURES AND TABLES

Figure 1 a & b	page 3
Figure 2 a & b	4
Figure 3 a & b	5
Figure 4	6
Figure 5 a, b, c, d	7
Figure 6 a	9
Figure 6 b	10
Figure 6 c	11
Figure 6 d	12
Figure 6 e	13
Figure 6 f	14
Figure 7	15
Figure 8	16
Figure 9	18
Table I	19

INTRODUCTION

In the previous quarterly reports^(1,2) we described the effects of hydrogen incorporation in r.f. sputtered amorphous GaAs on i) IR and Raman measurements, ii) the evolution of H_2 on heating, iii) electrical transport, iv) optical absorption and v) depth profiles of the constituent atoms. The effects of the variation of deposition parameters such as r.f. power, partial pressures of argon and hydrogen, substrate temperatures, T_s , etc. and also of post-deposition annealing treatments on the electronic properties as reported earlier^(2,3,4) highlighted three major problems encountered in a-GaAs:H alloys prepared by rf sputtering. These are i) onset of crystallization at T_s above 40°C, even though the amorphous films produced at a lower T_s could be annealed at much higher temperatures ($\sim 240^\circ\text{C}$) for a prolonged period without crystallization, ii) evolution of hydrogen ($\sim 2/3$ of the total hydrogen content of the film) at a rather low temperature ($\sim 130^\circ\text{C}$) and the associated degradation of the electronic properties and iii) deterioration of the properties for films deposited at high p_H and ambient temperature. Besides these problems, we have also witnessed evidence of microstructure/columnar growth in a-GaAs:H films prepared under certain conditions⁽⁴⁾. The presence of the microstructure is not unique either to a specific material as in this study or to a specific deposition process. It has also been reported in a-Si:H^(5,6) as well as a-Ge:H⁽⁶⁾ alloy films produced by glow-discharge decomposition and sputtering methods. However, as the structure - property correlation is quite intimate, we have undertaken a systematic approach to identify the deposition parameter - space suitable for a smooth, homogeneous film growth devoid of any observable microstructure. The results of such an endeavor to establish a deposition parameter - microstructure - property correlation in r.f. sputtered a-GaAs:H alloys will be presented here.

PREPARATION OF FILMS & MICROSTRUCTURAL CHARACTERIZATION

A description of the sample preparation technique and the sputtering apparatus/vacuum system has been given earlier⁽⁴⁾. The deposition parameters were: i) r.f. power (40 - 140 watts), ii) substrate temperature, T_s , upto 40°C, beyond which crystallization sets in, iii) partial pressures of hydrogen, p_H ($0 - 5 \times 10^{-3}$ Torr) and of argon, p_{Ar} ($5 - 15 \times 10^{-3}$ Torr). A number of samples were deposited simultaneously in the same deposition run for many parallel experiments. The results of the electronic^(2,3) and vibrational^(1,4) properties have already been reported. For the microstructural investigations by SEM and SIMS, the samples deposited on c-Si substrates (the same samples as used in IR measurements) were used. For the TEM and STEM measurements, samples of different thicknesses in the range between 400 - 1200 Å were deposited on carbon-coated microgrids. The SIMS analysis was done by Charles Evans Associates, California. Most of the SEM and TEM work was done (on a JSM35, JEOL unit) at the Materials Research Laboratory, Harvard University. A few SEM and STEM (100 CX, JEOL) measurements were performed at the JEOL facility, Natick, Massachusetts.

CORRELATION OF MICROSTRUCTURE WITH DEPOSITION PARAMETERS & ASSOCIATED

PROPERTIES OF FILMS

Depending on the partial pressures of the sputtering gases, the broad range of the deposition parameter space chosen in this investigation can be classified into four major categories: A) low p_H and low p_{Ar} , B) low p_H and high p_{Ar} , C) high p_H and low p_{Ar} and D) high p_H and high p_{Ar} . The other important deposition parameters such as, r.f. power and the substrate temperature could be variables too. Because of the limitation posed by the onset of crystallization at T_s above 40°C, all depositions were carried out on substrates held at ambient (room temperature) condition. The actual temperature of the film during growth could be much higher, of course, depending largely on the r.f. power, plasma conditions and substrate characteristics. The r.f. power was maintained constant at 140 Watts in one series of films produced with variable p_H and p_{Ar} . Another series of films were deposited at a fixed p_H and p_{Ar} [deposition conditions of Category A were chosen so that at low r.f. power there was no observable microstructure] but with varying r.f. power in the range between 80 and 300 Watts. The scanning electron micrographs (both in-plane and out-of plane or edge-on view) of the first series of films, which are representative of the four major categories A, B, C and D as mentioned above and are produced at fixed r.f. power, have been shown in Figures 1(a), 1(b); 2(a), 2(b); 3(a), 3(b) and 4, respectively.

Figures 5(a), (b), (c) and (d) show the normal incidence transmission electron micrographs of a different set of thinner films prepared under the above conditions specifically for TEM study. The samples belonging to category A, i.e. produced at low p_H and low p_{Ar} do not show any observable microstructure in either micrographs, the limits of resolution being $\sim 100\text{\AA}$ and, $\sim 10\text{\AA}$, respectively. The island structures seen in the films of category C are characterized by an average diameter $\sim 500\text{\AA}$, typical of the high p_H and low p_{Ar} films. The circumferential regions around these islands are usually smooth. The TEM measurements performed on similar samples of varying thickness showed no significant change in the dimensions of these islands, indicating that the film growth is perhaps columnar. The edge-on view shown in Figs. 3 and 4 clearly demonstrates that this columnar morphology extends all the way from the film-substrate interface to the bulk films of thicknesses as large as $\sim 12\mu\text{m}$. For certain deposition parameters, the surface micrographs show circular island structures or surface rings which correlate clearly with the columnar morphology seen in the edge-on view. However, for thin films or with deposition parameters, such as, low p_H and r.f. power the micrographs are homogeneously smooth with occasional appearance of isolated surface rings. Carefully controlled ion-milling of these isolated islands at successively incremental depths up to the substrate and subsequent SEM micrographs revealed that the ring structure as seen on the surface did not originate at the substrate-film interface for these films. The effect of variation of the r.f. power on the microstructure of a low p_H and low p_{Ar} (category 'A') film is shown in Figures 6(a), (b), (c), (d) and (e) for films deposited with 80, 140, 200,

Figure 1. Scanning Electron Micrograph of a-GaAs:H
 a) planar view b) edge-on view, Category A: low p_H and low p_{Ar}
 (top white layer is film, deposited on crystalline silicon substrate)

Figure 2. Scanning Electron Micrograph of a-GaAs:H
 a) planar view b) edge-on view, Category B: low p_H , high p_{Ar}
 (top white layer is film, deposited on crystalline silicon substrate)

Figure 3. Scanning Electron Micrograph of a-GaAs:H
 a) planar view b) edge-on view, Category C: high p_H and low p_{AR}
 (detailed, whitish-gray image is film, deposited on crystalline silicon substrate)

Figure 4. Scanning Electron Micrograph of a-GaAs:H
Category D: high p_H and high p_{Ar}

(b) Category B: low p_H , high p_{Ar}

(d) Category D: high p_H , high p_{Ar}

Figure 5. Transmission Electron Micrographs of a-GaAs:H

(a) Category A: low p_H , low p_{Ar}

(c) Category C: high p_H , low p_{Ar}

250, and 300 Watts of r.f. power and $p_H \sim 1 \times 10^{-3}$ and $p_{Ar} \sim 5 \times 10^{-3}$ Torr. At low r.f. powers the SEM micrographs are very smooth and homogeneous. At higher r.f. power occasional surface rings and few inclusions appear. This trend becomes intense at still higher power resulting in a "swiss-cheese" surface micrograph as shown in Fig. 6(e) for an r.f. power of 300 Watts. The composition of the "inclusions" was checked by microprobe analysis to be the same as in other areas of the film. We have done controlled ion-milling of these surface structures and taken SEM micrographs at higher magnification (18,000, instead of the usual ~ 6600 magnification). The edge-on view of the results as shown in Fig. 6(f) indicates that these structures are localized and do not extend to the substrate interface. The film deposited at the highest r.f. power of 300 Watts also showed columnar microstructure, though much smaller in dimension ($<100\text{\AA}$) than that presented in Figs. 3 or 4.

Caution must be exercised in the high resolution investigation of microstructures of thin films by intense electron beams. Spurious structures may be induced in the films due to electron beam heating effect. During the course of the investigation by STEM we have observed electron beam induced microstructure and resultant crystallization in a homogeneously smooth a-GaAs:H film. Fig. 7 shows the development of microstructures with the time of exposure to the electron beam. The well-resolved diffraction rings in the finally crystallized film are given in Fig. 8.

The large amount of evidence presented so far by the micrographs suggests a film growth via nucleation and coalescence of island structures. Columnar microstructure will become inevitable, if the coalescence is less than perfect. It is well known that the size and number of the nucleating centers are dependent on the rate of arrival and the energy of the depositing atoms, substrate temperature, electron bombardment of the film surface, etc. Both reduced rate of deposition at high p_H and a low T make the nucleus smaller (that is, lesser number of atoms in the cluster), thus increasing the possibility of well separated island structures in the films grown under such conditions. We have also observed occasionally growth of columnar microstructure in much thicker films ($\sim 10\mu\text{m}$) of Category B. Such a thickness induced microstructure may be attributed to the stress in the film. A state of stress is expected when a film is deposited on a substrate, if the thermal expansion coefficients of the film and substrate materials differ. However, over and above the stress resulting from the differential contraction, an intrinsic stress occurs in many materials. The magnitude of the intrinsic stress depends on the film thickness and substrate temperature and probably arises from features of the film structures. The stress may also vary with the depth in the film. Besides these, we must also keep in mind that with the removal of dangling bonds during the process

Figure 6a. Scanning Electron Micrograph of a-GaAs:H. Category A: low p_H , low p_{Ar} film deposited with 80 Watts r.f. power. Both planar and edge-on views are shown (top white layer is film, deposited on crystalline silicon substrate).

Figure 6b. Scanning Electron Micrograph of a-GaAs:H. Category A: low p_H , low p_{Ar} film deposited with 140 Watts r.f. power. Both planar and edge-on views are shown (top white layer is film, deposited on crystalline silicon substrate).

Figure 6c. Scanning Electron Micrograph of a-GaAs:H. Category A: low p_H , low p_{Ar} film deposited with 200 Watts r.f. power. Both planar and edge-on views are shown (top white layer is film, deposited on crystalline silicon substrate).

Figure 6d. Scanning Electron Micrograph of a-GaAs:H. Category A: low p_H , low p_{Ar} film deposited with 250 Watts r.f. power. Both planar and edge-on views are shown (top white layer is film, deposited on crystalline silicon substrate).

Figure 6e. Scanning Electron Micrograph of a-GaAs:H. Category A: low p_H , low p_{Ar} film deposited with 300 Watts r.f. power. Both planar and edge-on views are shown (top white layer is film, deposited on crystalline silicon substrate).

Figure 6f. Scanning Electron Micrograph of a-GaAs:H. Category A: low p_H , low p_{Ar} film deposited with 300 Watts r.f. power and with ion-milled surface examined under higher magnification. Both planar and edge-on views are shown (top white layer is film, deposited on crystalline silicon substrate).

Figure 7. Development of microstructure in a-GaAs:H with the time of exposure to the electron beam as seen by STEM. Arrows indicate new features.

Figure 8. Electron beam induced crystallization in a-GaAs:H as seen in STEM. Microstructure shown in top figure.

of hydrogenation the semiconductor network gets terminated, which means that the subsequent growth of the semiconducting film must circumvent the difficulty of going around such terminated bonds. Clustering of hydrogen atoms around such defects can easily be visualized. The deposition parameters such as high partial pressures of hydrogen and argon may thus inhibit coalescence of the nucleating islands resulting in a columnar morphology which extends through the film thickness. We observe that the column axes are approximately parallel to the growth direction; the island dimensions are not changed substantially and the surface rings are also present in materials without any resolvable columnar structure. The swiss cheese surface structures seen in Fig. 6(e) are quite instructive in the sense that the opening up of one of the holes and the creation of the blistered surface are shown in detail.

It has already been reported⁽³⁾ that almost 2/3 of the total incorporated hydrogen in a-GaAs:H alloys can be evolved at temperatures around $\sim 130^\circ\text{C}$. We believe that a large amount of this is due to unbonded/trapped hydrogen. It is then reasonable to assume that at high r.f. power (~ 300 Watts) the temperature of the growing film surface may become high enough to help the trapped hydrogen evolve through the top layers leaving behind gaping craters. We may thus identify the deposition parameter space needed for the growth of a homogeneously smooth a-GaAs:H film without any observable microstructure (Fig. 9).

Having established that variations do exist in the microstructure of a-GaAs:H films with changes in the deposition parameters, it is important to determine the extent of its effect on the electronic properties of the films. We have thus attempted the following microstructure - property correlation as given in Table I. As the samples were not sufficiently thick, estimation of E_{03} was difficult. The spectral dependence of the absorption edges showed evidence of increasing band tailing in the high p_H regimes. The data quoted in this Table I are the statistical representatives of a large number of samples measured in each category. The electrical properties, such as, the conductivity at room temperature (mho cm^{-1}), σ_{RT} ; the activation energy of electrical conduction (eV), E_a and the preexponential in the conductivity (mho cm^{-1}), σ_0 [as in $\sigma = \sigma_0 \exp(-E_a/kT)$] refer to samples annealed at 150°C for 1 hour. In all these samples, the electrical conduction does not show a single activated process for the full range of temperature investigated (425 - 100K). However, the data may be analyzed by a double activation mechanism, one at high temperature and the other at room temperature and below. The electrical activation energy in the low temperature region is typically ~ 0.20 eV. For the samples in category B, however, the contribution from the second process is negligibly small. The optical properties, such as, E_{04} and E_{03} , defined as the energies at which the absorption coefficient, α , are 10^4 and 10^3 cm^{-1} , respectively, and the photoconductivity, $\Delta\sigma$, measured at $h\nu \sim 1.96$ eV refer to the as-deposited films.

In so far as the microstructures are concerned, the results given in Fig. 9 and Table I can be summarized as follows: At high p_H i.e. in the categories C & D, the a-GaAs:H films exhibit columnar microstructures.

Fig. 9. The Deposition Parameter Space for Columnar Microstructure in r.f. sputtered a-GaAs:H alloys. The shaded area identifies the deposition parameters which provide observable microstructure in the films. Pressures, 2×10^{-3} Torr and above for high p_H and 10×10^{-3} Torr and above for the high p_{Ar} , demarcate the space.

TABLE I Microstructure - Property Correlation in a-GaAs:H films sputtered with 140 Watts r.f. power on room temperature substrates.

$\frac{P_H}{P_H + P_{Ar}}$ Properties	DEPOSITION PARAMETER SPACE			
	Category A low p_H , low p_{Ar} ~ 0.2	Category B low p_H , high p_{Ar} ~ 0.1	Category C high p_H , low p_{Ar} ~ 0.5	Category D high p_H , high p_{Ar} ~ 0.3
σ_{RT}	$\sim 10^{-6}$	$\sim 10^{-8}$	$\sim 3 \times 10^{-7}$	$\sim 2 \times 10^{-7}$
E_σ	0.52;0.18	0.68	0.47;0.19	0.50;0.22
σ_o	200; 2×10^{-4}	2×10^3	12; 4×10^{-4}	50; 9×10^{-4}
E_{04}	~ 1.30	~ 1.35	~ 1.35	~ 1.39
E_{03}	sharp edge	sharp edge	shallow	shallow
$\Delta\sigma$	4×10^{-9}	6×10^{-9}	$<10^{-9}$	1×10^{-9}

The associated changes in the properties are then to i) increase the conductivity, ii) decrease activation energy, iii) produce states (associated with ~ 0.22 eV) in the band gap, iv) decrease σ_0 , v) increase band tailing and vi) reduce photoconductivity.⁰ In effect, the properties deteriorate with the growth of columnar microstructure. Films in the category B appear to show the best properties.

CONCLUSIONS AND FUTURE PLANS

The microstructure - property correlation of a-GaAs:H alloys prepared by r.f. sputtering in a hydrogen-argon plasma leads to the following conclusions:

- i) There are a variety of microstructures in the films. Certain deposition conditions, such as, high p_H and p_{Ar} , tend to produce columnar microstructure which may extend through the film thickness. A low p_H and p_{Ar} , on the other hand, favor a smooth, homogeneous growth of the film without any observable microstructures. At high r.f. power the surface becomes blistered, probably through the evolution of hydrogen from the underlying film. The film growth, in general, proceeds via nucleation and coalescing of the island structure.
- ii) Several electronic properties such as electrical conductivity, activation energy of conduction, photoconductivity, absorption edge, etc. are adversely affected by the inclusion of the columnar microstructures.

The immediate future work has been proposed as:

- i) Preparation of chemically pure material at higher T and continued characterization by SEM, EIMS AND STEM analyses and IR observations.
- ii) Preparation at selected values of T , p_H , p_{Ar} and r.f. power to obtain materials with lower gap state density.
- iii) C-V and Schottky diode measurements to give the gap-state density and to evaluate the device potentials.

REFERENCES

1. Quarterly Technical Progress Report, Department of Energy, DOE/ET/23036-1, November 1979.
2. Quarterly Technical Progress Report, Department of Energy, DOE/ET/23036-2, March 1980.
3. W. Paul and D. K. Paul, SERI & DOE Amorphous Silicon/Materials Contractors' Review Meeting, Washington, D. C. April 1980, p. 107.
4. D.K. Paul, J. Blake, S. Oguz and W. Paul, J. Non-Cryst. Solids, 35 & 36, Parts I and II, 501 (1980)
5. J. C. Knights and R. A. Lujan, Appl. Phys. Letters, 35, 244 (1979).
6. R. Messier & I.S.T. Tong, SERI & DOE Amorphous Silicon/Materials Contractors' Review Meeting, Washington, D. C. April 1980.

DISTRIBUTION LIST

L. Guttman
Argonne National Laboratory
Solid State Science Division
Argonne, IL 60493

Battelle Columbus Laboratories
Attn: Dr. Alfred E. Austin
505 King Avenue
Columbus, OH 43201

Brookhaven National Laboratory
Dept. of Energy & Environment
Attn: R.W. Griffith
Upton, NY 11973

JILA
University of Colorado
Attn: A. Gallagher
Boulder, CO 80309

Institute of Energy Conversion
University of Delaware
Attn: Dr. Vikram Dalal
1 Pike Creek Center
Wilmington, DE 19808

Duke University
Department of Mechanical Engineering
Attn: Dr. Franklin H. Cocks
Durham, NC 27706

EIC Corporation
Attn: Dr. R. David Rauh
55 Chapel Street
Newton, MA 02158

Harvard University
Division of Applied Sciences
Attn: Dr. William Paul
Pierce Hall
Cambridge, MA 02138

Lawrence Berkeley Laboratories
University of California
Attn: Dr. Nabil Amer
Berkeley, CA 94720

Lockheed Missiles & Space Co., Inc.
Research & Development Division
Attn: Art Jonath
3251 Hanover Street
Palo Alto, CA 94304

Massachusetts Institute of Technology
The Energy Laboratory
Attn: Dr. David Adler
Cambridge, MA 02139

Mobil Tyco
Attn: M. Cretella
16 Hickory Drive
Waltham, MA 02154

Nval Research Laboratory
X-Ray Optics Branch
Attn: D.A. Papaconstantopoulos
Washington, DC 20375

Naval Research Laboratory
Semiconductors Branch
Attn: C. Taylor
Washington, D.C. 20375

Naval Weapons Center
Michelson Laboratory
Attn: Dr. T.M. Donovan
China Lake, CA 93555

Pennsylvania State University
Attn: Dr. R.F. Messier
265 Materials Research Laboratory
University Park, PA 16802

RCA Corporation
Attn: Dr. David E. Carlson
P.O. Box 432
Princeton, NJ 08540

Xerox Corporation
Attn: R.A. Street
3333 Coyote Hill Road
Palo Alto, CA 94304

Jet Propulsion Laboratory
PV Data Center
Attn: Leau Ann Burrus
MS 50241
4800 Oak Grove Drive
Pasadena, CA 91103