PRODUCTION AND EVALUATION OF a-GaAs SOLAR CELLS

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
AUGUST 1, 1979 - OCTOBER 31, 1979

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

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ABSTRACT

Alloys of a-GaAs with hydrogen have been prepared by r.f. sputtering in an argon atmosphere at several partial pressures of hydrogen and several substrate temperatures and r.f. power. Some films were deuterated. A suitable array of characterisational and property measurements has been instituted. The effect of isothermal annealing on electronic as well as vibrational properties has been studied. The correlation between the micro-structure and materials preparation parameters has also been investigated.

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 AND ROUTINE CHARACTERIZATION	2
EXPERIMENTAL MEASUREMENTS	3
RESULTS AND DISCUSSION	3
Vibrational Properties	3
Electronic Properties	5
Microstructure	8
CONCLUSIONS AND OUTLINE OF FUTURE WORK	9
REFERENCES	10
DISTRIBUTION LIST	11

LIST OF FIGURES

Figure 1	page 4
Figure 2	6

INTRODUCTION

In recent years the properties of amorphous semiconductors have been of great interest for both applied and fundamental considerations. While considerable effort has been expended in the study of both chalcogenides and elemental semiconductors, very little work has been done on amorphous III-V compounds. Research on "pure" tetrahedrally coordinated amorphous semiconductors has established that their properties are substantially determined by the characteristic presence of a high density of defect-related localized states in the energy gap. In the past several years various methods of preparation, viz. glow discharge decomposition of a molecule containing hydrogen, reactive sputtering or evaporation in hydrogen, ion implantation of hydrogen and annealing in an atmosphere of atomic hydrogen, etc., have been employed to reduce this gap state density. All of these methods result in the reduction of the gap state density through the compensation of dangling or weak reconstructed bonds by the incorporated hydrogen. Thus, hydrogenation is known to be important in reducing defect states and improving electrical and optical properties dramatically. Our earlier preliminary work⁽¹⁾ on the deliberate incorporation of hydrogen into a-GaAs prepared by the sputtering technique has shown similar results.

It is our intention, therefore, to carry out a comprehensive program encompassing sample preparation and characterization of structural, compositional, electrical and optical properties on a-GaAs:H alloys. The results of this study are expected to permit an evaluation of the potential of these amorphous materials for solar cells.

In this first quarterly report, the results of our investigations of the preparation and characterization of a-GaAs:H are presented.

PREPARATION OF FILMS AND ROUTINE CHARACTERIZATION

We have prepared alloy samples of GaAs of variable hydrogen content by r.f. sputtering in argon at several substrate temperatures and r.f. powers. We have also systematically varied the argon pressure of the sputter gas and have deliberately incorporated deuterium. A liquid nitrogen baffled turbo-molecular pump backed by a mechanical pump routinely produced a predeposition base vacuum of low 10^{-7} Torr in the sputtering system. The ambient in the sputtering enclosure was regularly subjected to residual gas analysis both before and immediately after sputtering. Water vapor has been found to be the major residual even after prolonged baking and pumping. The respective gas flows and the ratios were carefully monitored and controlled electronically. The five-inch diameter polycrystalline GaAs target (99.999%) was water-cooled during sputtering. Thin films deposited simultaneously on various substrates (Corning glass #7059, Be, crystalline Si-wedges, KBr, NaCl, metallized glass (Mo, Ni-Cr), etc.) were used for parallel experiments. Substrate temperatures above 40°C resulted in polycrystalline films. Alloys of a-GaAs:H have been dehydrogenated by heating in a separate series of experiments. Attempts to hydrogenate "pure" a-GaAs and to rehydrogenate previously dehydrogenated a-GaAs:H through exposure to a plasma of atomic hydrogen have not been successful.

Thicknesses ranging from a few thousand angstroms to several microns were measured directly by a Sloan Dektak. Also, other methods, e.g., positions of interference fringes in the near IR, a thin film optical constants program⁽²⁾ and a scanning electron microscope (SEM) have been used to estimate the thickness. The structural characterization was done by X-ray diffraction, SEM and TEM. The chemical composition of the films as checked by electron microprobe was within 1% of the target, and no significant amount of impurities was observed. The limiting accuracy of measurements by the energy dispersive SEM was of the same order. It should be mentioned, however, that traces of oxygen between 0.1 and 1 at. % have been detected recently by the SIMS analysis of hydrogenated amorphous silicon films prepared in the same sputtering system. Similar studies on a-GaAs:H have been planned. The hydrogen content of representative films has been determined by a method⁽³⁾ employing thermal evolution of hydrogen.

EXPERIMENTAL MEASUREMENTS

A variety of measurements were carried out on a number of samples which were deposited simultaneously on different substrates in the same preparational run. The measurements are:

- (1) d.c. conductivity as a function of temperature
- (2) a.c. conductivity as a function of temperature and frequency
- (3) absorption edge
- (4) vibrational absorption due to lattice and hydrogenic modes by infrared and Raman techniques
- (5) intensity and spectral dependence of photoconductivity
- (6) microstructure by TEM and SEM
- (7) photoluminescence.

The effect of isothermal annealing has been studied through repeated measurements of items as listed above in (1) to (6).

RESULTS AND DISCUSSION

1. Vibrational Properties of a-GaAs:H Alloys

A paper⁴ presented at the Eighth International Conference on Amorphous and Liquid Semiconductors (to be published in the Journal of Non-Crystalline Solids) includes a description of the following:

- (a) vibrational spectra as observed in the IR and Raman measurements
- (b) effect of dehydrogenation by annealing on the vibrational spectra
- (c) characteristics of hydrogen evolution upon heating
- (d) rehydrogenation in atomic hydrogen
- (e) microstructural growth examination by SEM.

The deliberate incorporation of hydrogen into a-GaAs has led to the introduction of a rich spectrum of hydrogen related localized vibrational absorption (Fig. 1). A very strong and sharp band occurs at $\nu \sim 530 \text{ cm}^{-1}$ and a strong but much wider band at $\sim 1470 \text{ cm}^{-1}$. In addition, several weak bands and a fairly strong reststrahlen absorption (corresponding to ω_{To}) were observed. Identification of the hydrogenic modes was made easier by comparing hydrogenated and deuterated samples. Introducing other gases, in addition to H_2 , while sputtering (N_2 , AsH_3 , for example) creates additional

Figure 1. IR transmission in pure and hydrogenated a-GaAs:H. Anneal times 1 hour.

bands in the vibrational spectra. Isothermal annealing at elevated temperatures (100°C and above) resulted in decreased vibrational absorption which can be associated with the evolution of hydrogen.

The evolution data (Fig. 2) typically showed two peak characteristics: (i) a strong peak at low temperature ($\sim 150^\circ\text{C}$) and (ii) a much weaker one at temperatures close to crystallization ($\sim 360^\circ\text{C}$). The evolution spectra, in general, are similar⁽³⁾ to those of a-Si:H, except that, in the latter case, the relative magnitudes of the two peaks are inverted. The integrated area under the first evolution peak amounts to approximately 70% of the total hydrogen content of the film. Its evolution at such a low temperature suggests that the hydrogen is rather weakly bound in the amorphous GaAs matrix. The effects of low temperature annealing on electrical and optical properties strongly support this conclusion.

2. Electronic Properties of a-GaAs Alloys

a. Absorption Edge

The optical constants (absorption coefficient and refractive index) have been evaluated mostly from the data of transmission measurements. Occasionally, both transmission and reflection data were utilized. The effects of the sample preparation parameters, such as substrate temperature, argon pressure, partial pressure of hydrogen, r.f. power and also, post-deposition thermal annealing (temperature and duration) on the optical constants have been studied systematically. The general trend of the absorption edge has been to shift to higher energy with increase in the partial pressure of hydrogen relative to the total pressure of the sputtering gas atmosphere. Annealing, on the other hand, which both heals network defects and may evolve hydrogen from the amorphous matrix by breaking bonds, produced a down-shift of the edge at elevated annealing temperature ($\sim 150^\circ\text{C}$). Increased hydrogenation by the variation of p_{H} from 0.2 to 5 mTorr during sputtering leads to an increase in the optical gap (E_{04}) from 1.1 to 1.4 eV. Dehydrogenation by thermal annealing reduces the gap by a few tenths of an electron volt. As the samples become polycrystalline for substrate temperature, T_s above 40°C , no shift in the absorption edge could be detected in the limited range of $40^\circ\text{C} > T_s > 4^\circ\text{C}$. Deposition at lower power, hence lower rate of deposition, produced an increased optical gap presumably due to more efficient compensation of the defect states.⁽⁵⁾

Figure 2. Evolution of hydrogen from a-GaAs:H. GaAs-29 was deuterated.
Insert: RGA of evolved gas.

The results can be analyzed in terms of the efficiency of incorporation of hydrogen into the amorphous network, and correlated with that of other parallel experiments on electron transport. A paper on this subject is being written up for publication.⁽⁶⁾

b. Photoconductivity

The spectral and illumination intensity dependences of the photoconductivity were measured at room temperature for a planar configuration of contacts. The magnitude of the photoconductivity under fixed conditions of illumination increased by about one order on hydrogenation, and the photoconductivity edge versus photon frequency shifted to higher frequencies (like the absorption edge). However, for an illumination flux of 10^{15} photons/cm²-sec at 1.96 eV, the photoconductivity $\Delta\sigma$ is only 6×10^{-9} ohm⁻¹-cm⁻¹, which may be compared with a-Ge:H alloys (our better values for these are of the order of 10^{-7} ohm⁻¹-cm⁻¹) and with a-Si:H (highest value $\sim 10^{-5}$ ohm⁻¹-cm⁻¹) under the same illumination conditions. The present much poorer photoconductivity of a-GaAs is evident. The reason is not understood yet, but its elucidation may help us understand the high values in a-Si:H as well as the low ones in a-GaAs:H.

c. Photoluminescence

Weak photoluminescence has been observed in some films of a-GaAs:H alloys measured at 77°K. The peak appeared around ~ 1.35 eV and is rather broad.⁽⁷⁾ These preliminary measurements are being extended presently.

d. Electrical Transport

We have assembled extensive data on conductivity and thermopower, as a function of measurement temperature and annealing temperature, for a matrix of a-GaAs:H alloys prepared at different partial pressures of argon and hydrogen; substrate temperatures, r.f. power, etc. Also, a.c. conductivity has been measured as a function of temperature and frequency. Computer programs have been developed to analyze both electrical conductivity and thermopower data, and derive a consistent model for the electronic transport. Analysis of these results leads to the following conclusions:

- (i) the conductivity decreases and the activation energy increases with increasing hydrogenation
- (ii) the temperature dependence of conductivity shows an activated process

at room temperature and above, and a hopping process at lower temperatures

- (iii) the activation energies derived from conductivity and thermopower data differ by as much as 0.2 eV
- (iv) the conductivity increases by more than an order of magnitude and the activation energy decreases due to hydrogen evolution by thermal annealing at $\sim 150^\circ\text{C}$
- (v) the a.c. conductivity shows a frequency dependence, $\sigma_{ac} \sim \omega^s$, where $s \sim 0.85$ at room temperature. The effect becomes larger at lower temperatures.

The above observations suggest the presence of defect/impurity states of significant density, besides the intrinsic network-derived bands. Parallel measurements of photoconductivity and optical absorption edges support this deduction. This work on carrier transport is being written up for publication. (9)

3. Microstructure of a-GaAs Alloys

The effect of deposition parameters, such as partial pressures of hydrogen and argon, r.f. power and substrate temperature, on the microstructure of the films has been studied by scanning and transmission electron microscope measurements. We have also attempted a correlation between the microstructures and the associated changes in several electronic properties of a-GaAs:H films. For certain deposition conditions, the surface micrographs show circular island structures which correlate clearly with the columnar morphology seen in the transverse plane (edge-on view). However, for thin films or deposition parameters such as low p_H and r.f. power, the microstructure is homogeneously smooth with occasional appearance of isolated islands on the surface. Controlled ion-milling of these islands and subsequent SEM revealed that the island structure as seen on the surface did not originate at the substrate-film interface. The micrographs suggest a film growth via nucleation and coalescence of islands. The deposition parameters, such as high r.f. power and high partial pressures of hydrogen or argon, inhibit coalescence of the nucleating islands resulting in a columnar morphology which extends through the film thickness. It has also been found that the films having columnar structures exhibit rather poor electronic properties, e.g. moderate dark conductivity, low photoconductivity, conductivity aniso-

tropy (between planar and sandwich configuration), very weak or no photoluminescence, and pronounced effect of annealing. A paper on this work is being prepared for publication.⁽¹⁰⁾

CONCLUSIONS AND OUTLINE OF FUTURE WORK

Amorphous GaAs:H alloys have been made by r.f. sputtering in an argon-hydrogen atmosphere, and several of the characterization measurements performed: SEM and TEM examination, thickness, X-ray diffraction, optical absorption in the visible and IR regions, Raman scattering, photoconductivity, photoluminescence and electrical transport. The effect of thermal annealing on the electrical, optical and microstructure have been studied. Also, an attempt has been made to correlate the preparation parameters and the properties with the microstructure.

The immediate future work is proposed along the following lines:

- (i) preparation of chemically pure material (no O) as tested by SIMS analysis and IR absorption
- (ii) preparation of material with a reduced density of weakly-bonded H, which is a suspected cause of high gap state density
- (iii) continued study of the photoconductivity of the new material, in a search for necessary increases by orders of magnitude
- (iv) continued characterization by photoluminescence
- (v) initiation of capacitance-voltage measurements.

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