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PRODUCTION AND EVALUATION OF a-GaAs SOLAR CELLS

FINAL TECHNICAL REPORT
FOR THE PERIOD
August 1, 1979 - July 31, 1980

✓ William Paul, Principal Investigator
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ABSTRACT

Alloys of GaAs with hydrogen have been prepared both by r.f. sputtering in argon and by glow discharge decomposition of mixtures of AsH_3 and $\text{Ga}(\text{CH}_3)_3$. Many deposition parameters have been systematically varied: argon pressure, hydrogen pressure, substrate temperature, sputtering r.f. power. Among the characterizational methods employed have been X-ray diffraction, transmission and scanning electron microscopy, electron microprobe, secondary ion mass spectrometry and hydrogen evolution. The properties measured, usually on co-deposited samples, included conductivity and thermopower as a function of temperature, optical absorption edge, vibrational optical absorption in the infrared, Raman scattering, electron spin resonance and photoconductivity. Samples constructed in Schottky barrier configurations were also studied and capacitance-voltage, field effect and photoluminescence experiments carried out. The possibility of doping with Si, and of temperature stabilization by various means was explored. Finally the production of many samples over the wide variety of preparational conditions, their fundamental properties as indicated, and the usual device studies were evaluated in toto in order to assess the present potential of a-GaAs:H for solar cells. It was concluded that this material probably shares with other hydrogenated binary compounds the fundamental flaw that, despite clear signs of the effects of hydrogen in reducing the density of gap states, there still remains too high a density for viable devices to emerge. Suggestions are made for new studies likely to clarify the present difficulties.

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.

I. INTRODUCTION

The objective of this program was to produce and dope amorphous GaAs:H alloys, and to evaluate their potential for low-cost solar cell material. The approach to be adopted was to r.f. sputter GaAs in the presence of H_2 and dopant gases such as PH_3 and B_2H_6 , and to vary the conditions of preparation such as substrate temperature T_s , hydrogen partial pressure p_H , argon sputtering gas pressure p_{Ar} , r.f. sputtering power and gas flow rate. The films were to be characterized chemically and structurally through measurements of H-content (secondary ion mass spectroscopy, H-evolution, infrared vibrational absorption), transmission and scanning electron microscopy, electron microprobe and X-ray diffraction. Property measurements on co-deposited samples were to be carried out: infrared vibrational absorption, absorption edge, conductivity and thermopower as a function of temperature, photoluminescence, photoconductivity as a function of photon energy and temperature, electron spin resonance and Raman scattering. Finally, all of these measurements were to be correlated among themselves and with the preparation conditions, and an assessment made of the future potential of the material. Elementary device structures such as Schottky barriers were planned as a direct evaluation of this potential.

This program has been carried out in the full detail of the paragraph above. In addition, a-GaAs:H has been produced by the glow-discharge decomposition of mixtures of AsH_3 and $Ga(CH_3)_3$ at several substrate temperatures. The conclusions on evaluation of a massive array of data are that this material shares with other amorphous binary alloys with hydrogen the flaw of a large density of states in the pseudogap. The usual indicators of H-compensation of dangling bond defects are evident: enlarged optical energy gap (over unhydrogenated material), reduced conductivity and spin resonance, improved photoconductivity. Nevertheless, the improvement in photoelectronic properties is inadequate for a confident prognosis of the construction of a useful device.

Consideration of the general binary problem has suggested that the difficulty lies, at least in part, in the preference shown by H for one of the elements of any binary in the film-formation process. This leaves defects on the unpreferred element uncompensated and necessarily gives a higher gap state density than in the alloy of Si with H. Experiments to test this thesis are being done, but the preliminary results overwhelmingly favor the correctness of the thesis.

The arrangement of this Final Report will take account of the facts that some of the material has been fully discussed in three quarterly reports and some has been submitted for publication.

II. CONDITIONS OF PREPARATION

The preparation of the films by r.f. sputtering was discussed in our first Quarterly Report [1] and was published separately [2]. Films were also produced by the glow discharge decomposition of mixtures of AsH_3 and $Ga(CH_3)_3$. The latter method will now be briefly described.

A d.c. glow discharge apparatus was built from quartz glass and stainless steel components. The pumping system consisted of a liquid nitrogen

cold trap, a diffusion pump and a roughing pump. During deposition the diffusion pump was bypassed. The adjustable electrode gap was set at 13 mm. The voltage applied was between 700 and 900 volts, and the plasma current ranged between 0.2 and 1.4 mA, depending on the gas composition and line pressures. The stainless steel substrate platform could be heated to 400°C. Mixtures of pure gases (arsine, electronic grade, Mathieson, Massachusetts, and trimethyl gallium (TMG), Alfa Industries, Massachusetts, 99.9995%, electronic grade) were discharged in the glass reaction chamber. The partial pressure of AsH₃ was varied between 90 and 180 mTorr, while the composition was changed by varying the ratio of pressures of AsH₃ and TMG between 0.2 and 1.0. Because of the high vapor pressure of TMG at room temperature, a carrier gas like H₂ was bubbled through the TMG cylinder, which was kept in ice.

III. CHARACTERIZATION

A. Amorphicity

The amorphous nature of the films was tested by X-ray diffraction techniques. One of the major problems encountered in a-GaAs:H alloys prepared by r.f. sputtering has been the onset of crystallization at substrate temperatures, T_s , above 40°C, even though the amorphous films produced at lower T_s could be annealed at much higher temperatures (at least 240°C) for a prolonged period without any crystallization [2,3,4]. Deposition at lower r.f. power (40 watts instead of the usual 140 watts) and/or varying partial pressures of H₂ or Ar did not improve the situation [5]. This problem limited the deposition temperature of the amorphous films produced by r.f. sputtering. However, using the glow discharge decomposition method, it has been possible to produce amorphous GaAs:H alloys at $T_s = 200^\circ\text{C}$.

B. Microstructure

We have seen evidence of microstructure/columnar growth in r.f. sputtered a-GaAs:H films prepared under certain conditions [1,2,4,5]. The presence of microstructure in thin films is not unique either to a specific material or to a specific deposition process. It has also been reported in a-Si:H [6,7] and a-Ge:H [7] 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-properties correlation in r.f. sputtered a-GaAs:H alloys were reported fully in a Quarterly Report [5]. Here we give only some summary remarks.

Many deposition parameters, such as partial pressures of hydrogen, p_H , r.f. power, P_{rf} , substrate temperature, T_s , target to substrate distance, geometry of the sputtering apparatus, etc., play important roles in the nucleation, growth, microstructure and properties of sputtered thin films. 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 temperature. The actual temperature of the film during growth could be much higher,

depending largely on P_{rf} , plasma conditions and substrate characteristics. The geometry was also kept fixed, the target to substrate distance being 7 cm. In one series of films P_{rf} was maintained constant at 140 watts while p_H was varied between 0 and 5 mTorr and p_{Ar} between 5 and 15 mTorr. In another series P_{rf} was varied while p_H and p_{Ar} were kept constant.

It is convenient to classify the microstructures observed by dividing the deposition parameter space into four sections (Fig. 1). Thus, high p_H and p_{Ar} tend to produce columnar microstructure which may extend through the film thickness. On the other hand, low p_H and p_{Ar} favor a smooth, homogeneous growth of the film without any observable microstructure. 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. We may mention here that several electronic properties are adversely affected by the presence of columnar microstructures. This will be described in Section V.

C. Chemical Composition

The gross composition of the films was determined by electron microprobes with an overall accuracy of $\pm 2\%$. One of the microprobes was equipped with a wavelength analyzer and computer-interfaced to take account of various correction factors, such as background, matrix effect, etc., in the quantitative analysis. The average composition was checked to be uniform across the film and was within 1% of the target composition (polycrystalline, stoichiometric, Cr-doped GaAs target, 99.999% purity) for the sputter-deposited films [2]. The Secondary Ion Mass Spectrometric (SIMS) analysis (Charles Evans Associates, California) of the films provided information on the variation with depth of the relative concentration of various constituents. In principle, it is also possible to obtain the absolute concentrations of the constituents from the SIMS analysis, but the sensitivity factors of different elements in SIMS analysis depend strongly on the atomic matrix of the sample. Thus, any quantitative compositional data by SIMS must be based on standards of similar composition. In the absence of such standards and also because of other instrumental limitations, we rely on the electron microprobe data for the composition of the samples (particularly, glow discharge a-GaAs:H films) reported here.

Figure 2 shows SIMS data using an O^+ source. Significant amounts of Al ($\sim 10^{18} \text{ cm}^{-3}$) and Cr ($\sim 4 \times 10^{16} \text{ cm}^{-3}$) can be seen. These results are understandable, since Al is the major impurity (0.1 ppm) in both Ga and As of 99.9999% purity. Also, the GaAs target was semi-insulating, and this is usually achieved by Cr doping. Figure 2 demonstrates the important features that the hydrogen is uniformly distributed throughout the film thickness and there is no build-up of contaminants at the film-substrate interface. The depth profiles of the constituents indicate the homogeneity of the material deposited from a compound target by the sputtering process. A report on this subject has been presented earlier [5].

D. Hydrogen Content

There are four principal techniques employed to determine the hydrogen content in amorphous semiconductors. They are:

Figure 1. 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. The demarcation lines are at $p_H = 2$ mTorr and $p_{Ar} = 10$ mTorr.

Figure 2. SIMS depth profiles. At an ion intensity of 1×10^6 counts/sec, each ion will have a concentration of $^1\text{H} \approx 9 \times 10^{22} \text{ cm}^{-3}$, $^{27}\text{Al} \approx 3 \times 10^{18} \text{ cm}^{-3}$, $^{52}\text{Cr} \approx 8 \times 10^{18} \text{ cm}^{-3}$ and $\text{C} \approx 4 \times 10^{21} \text{ cm}^{-3}$. The intensity of ^{71}Ga was too large to analyze using the same conditions as above. The Ga profile was as uniform as other elements with the normalized ion intensity at $\sim 4 \times 10^7$ counts/sec.

- (i) IR absorption: the bonded H-content is estimated from the strength of the IR absorption bands due to the host atom-H vibrations. A quantitative relation must first be established between the integrated absorption (over frequency) of a particular vibrational mode and the hydrogen concentration, through calibration using an absolute method.
- (ii) Nuclear resonance: this is an absolute calibration procedure based on the nuclear reaction between the hydrogen in the film and a beam of high energy ions, such as ^{15}N , from an accelerator. This method may also provide depth profiling, by varying the energy of the incident ion beam.
- (iii) Thermal evolution of H: in this method a known mass of sample is heated in vacuum and the increase in pressure in an enclosure of known volume, when all of the H has been evolved, is used to estimate the atomic percentage of bonded and unbonded H. This estimate may be low because of H-diffusion into the walls of the enclosure and retention of H in the crystallized film.
- (iv) SIMS analysis: secondary ion mass spectrometric analysis using a suitable ion source (Cs^+ or O^+) provides quantitative measures of the composition of films as a function of position between film surface and film-substrate interface. The accuracy of this measurement is dependent on the availability of standards of composition similar to that of the sample.

In the present investigation of a-GaAs:H films, methods (i), (iii) and (iv) have been used. Though IR absorption has been systematically measured, lack of any suitable relationship between the integrated absorption and the H-content of the films measured by another method has limited the full utilization of the IR data [1,2]. The data from SIMS analysis [5] have been discussed in Section III-C. The characteristics of H-evolution upon thermal heating have been reported previously [1]. The evolution data (Fig. 3) 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 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 in a-GaAs:H amounts to approximately 70% of the total H-content of the films. Its evolution at such a low temperature suggests that the incorporated H is rather weakly bound in the amorphous GaAs matrix. The effects of low temperature annealing on electrical and optical properties [3] strongly support this conclusion.

IV. VIBRATIONAL ABSORPTION

The vibrational absorption spectrum of Ga-H and As-H bonds, and its modification with annealing at temperatures up to 150°C , were described in a Quarterly Report [1] and a paper [2]. The features in the absorption are much broader than in a-Si:H, presumably because of the wide variety of local environments for the vibrating complex, so that an unambiguous identification is somewhat difficult. We have, however, compared the vibrational absorption in the regions appropriate to the hydrogenated and deuterated GaAs, and observed the frequencies scale roughly as $1/\sqrt{2}$, which is strong evidence that these features are due to hydrogenic vibrational modes. Also, annealing at temperatures above 100°C resulted in decreased absorption, which can be reasonably associated with the evolution of H. Figure 4 is typical of the results. A comparison of the IR and Raman data with the established vibrational frequencies of known related hydrogenated compounds helps in the assignment of these modes (Table 1).

Figure 3. Evolution of hydrogen from a-GaAs:H. GaAs-29 was deuterated.
Insert: RGA of evolved gas.

Figure 4. IR transmission in pure and hydrogenated a-GaAs:H. Anneal times 1 hour.

Table 1. Vibrational bands in a-GaAs:H

INFRARED						RAMAN		COMMENTS
GaAs		GaAs:H		GaAs:D:H		GaAs:H		
Frequency (cm ⁻¹)	Integrated Absorption (cm ⁻²)	Frequency (cm ⁻¹)	Integrated Absorption (cm ⁻²)	Frequency (cm ⁻¹)	Integrated Absorption (cm ⁻²)	Frequency (cm ⁻¹)	Normalized Intensity	
258	2.9 × 10 ⁵	258	2.7 × 10 ⁵	256 185	2.7 × 10 ⁵	256	0.3	TO
526	1.8 × 10 ⁴	530	3.0 × 10 ⁴	526(H) 375(D)	2.5 × 10 ⁴	530	0.6	2TO: Hydro- genic Mode
		840		835(H) 595(D)		850	0.3	Hydrogenic Mode (Deformation)
		1008		730(D)		1007	0.6	As-H (Deformation)
		1480	3.7 × 10 ⁵	1475(H) 1050(D)	2.6 × 10 ⁵	1486	0.8	Hydrogenic Mode (Stretch)
		1780		1795(H) 1285(D)				Ga-H (Stretch)
		2060						As-H (Stretch)
		2135		1540(D)		2120	1.0	As-H (Stretch)

V. ELECTRONIC PROPERTIES

In the second Quarterly Report [3] we described the effects of H incorporation on the electrical transport and optical absorption of r.f. sputtered amorphous GaAs. The measurement and data reduction techniques and the apparatus were also discussed [2,3]. The results for the dependence of the electronic properties on various deposition parameters and post-deposition annealing treatments will be briefly reviewed here and a paper on this subject will be published elsewhere.

A. Effects of H-incorporation

H-incorporation modifies both the electrical and optical properties by reducing the density of defect states. However, the changes are never as great as in the case of a-Si:H alloys. It should be remembered that the substrate T_s is limited to $T_s \leq 40^\circ\text{C}$ by the crystallization process, and even a-Si:H films do not display very good properties when deposited at low temperature. Also, the electrical conduction in a-GaAs:H does not show a single activated process for the full range of temperature investigated here (425 to 100 K). However, if we choose to analyze the temperature-dependence of the electrical conductivity by activated mechanisms, we may identify two regions of activated conduction, one at high temperature and the other at room temperature and below. In order to find these energies, we have given a least squares fit (error less than $\pm 0.5\%$) to the conductivity data (typically varying over two to three orders of magnitude) in the respective temperature ranges. Using this two-band model, both thermoelectric power and conductivity data have been analyzed.

It is evident that increasing p_H leads to a decrease in the conductivity at all temperatures and an increase in the activation energy for conduction (Figures 5 and 6). This trend continues up to certain values of p_H , beyond which the trend reverses. See, for example, Figure 6. The trend is consistent with a decrease, followed by an increase, of gap state density with p_H .

The optical absorption edge spectra are consistent with this. Figure 7 illustrates a shift and sharpening of the edge as p_H is first increased, but a shallower edge is found for the highest p_H of the figure. The photon energy corresponding to $\alpha \geq 10^4 \text{ cm}^{-1}$ continues to increase at all p_H , probably indicating that the main valence band-conduction band gap is increasing. However, the shallower absorption edge between 10^3 and 10^4 cm^{-1} may be taken to reflect an increase in the density of states in the pseudogap. These results are further illustrated in Figure 8.

B. Effects of Annealing

The effects of annealing on the electronic properties were extensively studied. In general, thermal annealing heals defects and removes states from the pseudogap. However, if H is evolved, the breaking up of already satisfied dangling bonds may lead to the creation of defects and an increase in gap state density. The net results of these competing processes depend on the initial degree of hydrogenation and the annealing temperature, and may be discerned in an examination of Figures 5 and 6. Annealing at a relatively low temperature (near 100°C) usually decreases σ , as defects are

Figure 5. The temperature dependence of the electrical conductivity: effects of p_H and isothermal annealing on films deposited at high r.f. power. (a) as-deposited; (b) annealed at 100°C for one hour; (c) annealed at 150°C for one hour. $P_{rf} = 140$ watts; $p_{Ar} = 10$ mTorr; p_H in the samples #36 = 1: 5, #36-2: 2.6, #36-3: 1 and #36-4: 0.2 mTorr.

Figure 6. Room temperature conductivity and electrical activation energy as a function of the p_H/p_{total} . p_{total} is the sum of variable deposition parameters, p_H and p_{Ar} .

Figure 7. Absorption edge in a-GaAs:H for various p_H . Insert: α vs $h\nu$ over a large energy range for a film deposited at high p_{Ar} . Dashed curve: $p_H = 0$.

Figure 8. The effects of the sputtering gases p_H and p_{Ar} on the optical properties: as-deposited films. The photon energies E_{04} and E_g are defined respectively by the absorption coefficient, $\alpha = 10^4 \text{ cm}^{-1}$, and by the relation $(\alpha h\nu)^{1/2} = B(h\nu - E_g)$. P_{total} is the sum of variable deposition parameters, p_H and p_{Ar} .

healed and H is not yet evolved. Higher temperature annealing ($> 150^{\circ}\text{C}$) usually leads to an increase in σ , almost surely because of the H-evolution seen in separate experiments.

The effect of annealing on the optical properties is consistent with the two tendencies described above. Thus, the optical gap E_{04} increases with annealing for samples prepared at small $p_{\text{H}}/p_{\text{total}}$ - representing the dominance of, first, the healing effect, and, second, the effect of H-evolution.

As seen in Figure 9, an extended annealing treatment at 125°C for a period of three hours is not sufficient to arrest the above mechanisms in this material. However, annealing at 150°C for a period of three hours appears to have produced a metastable value for the optical gaps. Successive annealing at very high temperatures (up to 240°C) does not lead to any further observable change in the optical gaps.

The electronic properties typical of well-annealed ($T_{\text{A}} \sim 150^{\circ}\text{C}$) a-GaAs:H alloys are: an optical gap (E_{04}) of ~ 1.3 eV; a p-type conduction with an $S \sim 0.8$ mV/ $^{\circ}\text{K}$ at room temperature and conductivity activation energies of 0.65 and 0.2 eV, respectively, for the high and low T regions.

C. Correlation of Structure and Properties

The dependence of electrical transport and optical absorption on the incorporation of H, and on annealing, may be explained in terms of modifications in the gap state density in a manner similar to that used in the analysis of a-Si:H alloys. As in the latter case, the high temperature transport may be inferred to be in an intrinsic conduction band, despite the fact that the measurements were not carried to very high temperatures. The low temperature transport may or may not be activated, but very likely involves only states in the gap, whose density (and the related transport) is higher in samples produced at low p_{H} and left unannealed. Consistent with this picture, the position and shape of the optical absorption edge are determined by the incorporated H which both modifies the valence band edge and the concentration of defect states in the gap.

The changes in the electronic properties at high p_{H} are very likely related to the clearly-established growth of columnar microstructure. The variations in microstructure with deposition conditions were discussed in Section III.B. The differences in electronic properties of films deposited in the four quadrants of deposition-parameter space of Figure 1 are given in Table 2. A special remark may be made on the electrical transport of samples in category A. These were prepared at low p_{H} , yet show the highest conductivity, and low E_{04} . Unlike the samples of categories C and D which also show high conductivity, they do not show any microstructure. Thus, the high σ (high gap state density) is probably connected with an insufficiency of H to compensate the dangling bonds.

In summary, if indeed these differences in the electronic properties are properly to be assigned to the microstructural changes, it appears that increased microstructure (i) increases the conductivity, (ii) decreases the conductivity activation energy, (iii) introduces states in the effective band gap, (iv) decreases σ_0 , (v) increases band tailing, and (vi) reduces the photoconductivity.

Figure 9. The effect of isothermal annealing on the optical properties: variation with annealing time and temperature. Sample #35-1 has been annealed at 150°C for 3 hours without any preannealing at lower temperature.

Table 2. Microstructure-Property Correlation in a-GaAs:H films sputtered with 140 Watts r.f. power on room temperature substrates.

Properties	DEPOSITION PARAMETER SPACE			
	Category A low p_H , low p_{Ar} $p_H/p_H+p_{Ar} \sim 0.2$	Category B low p_H , high p_{Ar} $p_H/p_H+p_{Ar} \sim 0.1$	Category C high p_H , low p_{Ar} $p_H/p_H+p_{Ar} \sim 0.5$	Category D high p_H , high p_{Ar} $p_H/p_H+p_{Ar} \sim 0.3$
σ_{RT} (mho cm^{-1})	$\sim 10^{-6}$	$\sim 10^{-8}$	$\sim 3 \times 10^{-7}$	$\sim 2 \times 10^{-7}$
E_G (eV)	0.52; 0.18	0.68	0.47; 0.19	0.50; 0.22
σ_0 (mho cm^{-1})	200; 2×10^{-4}	2×10^3	12; 4×10^{-4}	50; 9×10^{-4}
E_{04} (eV)	~ 1.30	~ 1.35	~ 1.35	~ 1.39
Absorption edge	sharp	sharp	shallow	shallow
$\Delta\sigma$ (mho cm^{-1})	4×10^{-9}	6×10^{-9}	$< 10^{-9}$	1×10^{-9}

The electrical properties, such as the conductivity at room temperature, σ_{RT} ; the activation energy of electrical conduction E_G and the pre-exponential factor, σ_0 [as in $\sigma = \sigma_0 \exp(-E_G/kT)$] refer to samples annealed at 150°C for one hour. The optical properties, such as E_{04} , defined as the energy at which the absorption coefficient, α , is 10^4 cm^{-1} , and the photoconductivity, $\Delta\sigma$, measured at $h\nu \sim 1.96 \text{ eV}$, refer to the as-deposited samples.

VI. INHIBITION OF H EVOLUTION AT LOW TEMPERATURE

Three identifiable major problems encountered in r.f. sputtered a-GaAs:H alloys are: (i) onset of crystallization at nominal substrate temperatures above 40°C, even with r.f. power as low as 80 Watts. In the sputtering process the actual temperature of the growing film is most likely to be much higher than the measured nominal temperature and is dependent on several parameters, such as r.f. power, thermal properties of the substrate, gas flow conditions, etc.; (ii) deterioration of the properties for films having observable microstructures, and (iii) evolution of H, approximately two thirds of the total H content of the films, at a rather low temperature (~ 130°C) and the associated degradation of the electronic properties.

However, using the less energetic deposition process of glow discharge decomposition of $\text{Ga}(\text{CH}_3)_3$ and AsH_3 in a carrier gas of hydrogen, we have been successful in producing a-GaAs:H alloys at a nominal T_s of 200°C, which is presumably closer to the actual temperature of the growing film. The second problem may be avoided by choosing deposition parameters which do not introduce observable microstructure. To address the third problem of stabilizing the incorporated H in the r.f. sputtered amorphous GaAs matrix, it appears that there may be at least two possible approaches. The first is to produce the films at low r.f. powers (40-80 watts) in Ar-H atmospheres, with the expectation that the low deposition rate and ion energies may lead to a film structure less likely to accommodate weakly bonded H. The second possibility is an unexpected outcome of our investigation of the Si doping of a-GaAs:H through the addition of SiH_4 gas to the Ar-H plasma during film production at our normal r.f. powers of 140 watts.

This section of the report will describe in more detail our studies of low r.f. power depositions and of Si-doped GaAs. The most direct evidence of the stabilization of H-content is obtainable from measurements of H-evolution on heating. Less direct evidence is afforded by the results of annealing on electronic properties, such as the electrical conductivity, and optical properties, such as the vibrational absorption in the infrared region of the spectrum.

A. Samples Produced at Low r.f. Power

Films were produced at an r.f. power of 80 watts instead of the usual 140 watts, while the H partial pressure was varied between 0.2 and 2.6×10^{-3} Torr. The effects of annealing on the infrared vibrational absorption and the electrical conductivity were then studied. The changes on annealing appear to be smaller than those for films prepared at high r.f. powers but otherwise identical conditions of argon and hydrogen partial pressures. This suggests that the H in the low P_{rf} films is more stable. Unfortunately it was not possible to perform evolution studies.

Figures 10(a), (b) and (c) show some illustrative results. Figure 10(a) shows the effect on $\log \sigma$ vs $1/T$ of successive anneals at 150°C and 200°C. Figure 10(b) gives the characteristics for films as-deposited at different values of p_{H} , and Figure 10(c) shows these characteristics after the films had been annealed at 200°C. In this figure a plot for a film deposited at high r.f. power is included for contrast.

From Figure 10(b) it is seen that σ decreases monotonically as p_{H} is increased from 0 to 2.6×10^{-3} Torr. Annealing at 200°C increases σ_{H} for

(a)

(b)

(c)

Figure 10. The temperature dependence of the electrical conductivity: effects of p_H and isothermal annealing on films deposited at low P_{rf} (80 watts) and $p_{Ar} = 5$ mTorr. (a) high p_H , 2.6 mTorr; (b) as-deposited and (c) annealed at 200°C for one hour. GaAs #35-2 is a 140 watt, $p_H = 1$ mTorr film annealed at 150°C for one hour.

films deposited with $p_H > 10^{-3}$ Torr and decreases σ for those with $p_H \leq 0.8 \times 10^{-3}$ Torr. This is consistent with the supposition that the main effect of annealing for films of low H-content is to heal defects, while that for films of high H-content is to evolve H and cause defects. After anneals at 200°C, all of the samples show closely similar σ vs $1/T$ (see Figure 10(c)).

Although it appears, from the different behavior under annealing of the films deposited at different p_H , that H is being evolved, it is to be noted that the overall changes in σ are small, and are significantly smaller than those found for films deposited at high r.f. powers. Film 35-2 (Figure 10(c)) which was prepared at high P_{rf} but comparable p_H and p_{Ar} , illustrates this observation.

B. Si-doped GaAs:H and GaAs:Si:H Alloys

In this section we shall report a reduction of H evolution in GaAs:Si:H alloys compared with GaAs:H, and take occasion to include other properties of these materials.

The alloys were prepared by sputtering a GaAs target at an argon pressure of 5×10^{-5} Torr in partial pressures of SiH_4 of 0, 5×10^{-5} , 2.5×10^{-4} , 5×10^{-4} and 10^{-3} Torr. The corresponding Si contents were 0, 4, 5, 10 and 25 atomic % and are included in Table 3, which summarizes the chemical characterization and the optical and electrical results.

1. Evolution

Experiments on the thermal evolution of H do not show the first peak near 130°C characteristic of samples which do not contain Si. See Figure 11. It is pertinent to note that a sample containing 4 atomic % Si also included at least 9 atomic % H. This figure is a lower bound because the experiment on H-evolution was not carried to completion, in order to avoid possible As dissociation above 500°C and consequent contamination of our evolution apparatus. As a result, the absence of the first evolution peak cannot be attributable wholly to the attachment of the H preferentially to the Si.

2. Electrical and Optical Properties

a. Infrared absorption

The incorporation of Si into a-GaAs gives an additional infrared absorption peak near 385 cm^{-1} , which is quite sharp ($\sim 20 \text{ cm}^{-1}$ half-width) for low (4 at. %) Si concentration, but becomes broad and shifts to lower frequency ($\sim 370 \text{ cm}^{-1}$) at higher concentration (25 at. %). For comparison, incorporation of Si into crystalline GaAs [8,9] leads to localized modes at 384 and 369 cm^{-1} . The former is attributed to Si substituting for a Ga atom (Si_{Ga}) and the latter to a ($Si_{Ga} - V_{Ga}$) defect pair. Here V_{Ga} denotes a vacancy on a Ga site. Other neutral defects, such as ($Si_{Ga} - Si_{As}$) have been identified with infrared absorption bands at 367, 393 and 464 cm^{-1} . However, we have observed no new features near 460 cm^{-1} for the amorphous matrix.

Other modes, clearly identifiable as Si-H stretching and wagging vibrations, have been observed. None of the H-induced vibrational absorption

Figure 11. Effect of Si doping on the evolution of H from a-GaAs:H alloys. $P_{rf} = 140$ watts.

Table 3. Properties of silicon doped, r.f. sputtered a-GaAs:H alloys.
 T_s = ambient temperature, r.f. power = 140 watts, $p_{Ar} = 5 \times 10^{-3}$ Torr

Samples a-GaAs:H	Deposition Parameters		Thickness (μm)	Microprobe Data (atomic %)			σ_{RT} ($\Omega \text{ cm}$) ⁻¹ as-dep.	E_σ (eV) 200°C ann.	σ_o ($\Omega \text{ cm}$) ⁻¹ 200°C ann.	E_{03} (eV) as-dep.	E_{04} (eV) as-dep.
	P_H (10 ⁻³ Torr)	P_{SiH_4} (10 ⁻³ Torr)		Ga	As	Si					
471	1	0.05	2.30	47	48	5	1×10^{-7}	0.62	2.1×10^3	1.05	1.29
472	1	0.25	2.75	48	46	6	1.3×10^{-7}	0.62	4.0×10^3	1.01	1.30
473	1	0.50	2.70	46	44	10	4×10^{-7}	0.58	2×10^3	0.99	1.29
474	0	1.0	2.60	38	37	25	3.6×10^{-7}	0.54	1.2×10^3	0.95	1.22
522	1	0.05	3.15	49	47	4	1.2×10^{-7}	0.61	1.8×10^3	1.01	1.25
523	1	0.25	3.45	48	47	5	2.5×10^{-7}	0.58	1.6×10^3	0.98	1.25
524	0	0.50	2.85	48	46	6	2.3×10^{-6}	0.57	1.0×10^3	0.90	1.16
352	1	0	1.20	50	50	-	5.8×10^{-8}	0.56	1.2×10^3	1.18	1.32

features are affected by annealing at temperatures near 200°C. This is then consistent with the findings of the experiments on H-evolution on heating.

b. Electrical conductivity

The effect of annealing on the temperature dependence of the conductivity (Figures 12(a) and (b)) of the as-deposited samples (ambient temperature) is not observable at temperatures as high as 200°C for the low p_{SiH_4} films. For the highest p_{SiH_4} films, there was a very small increase in the electrical conductivity at low temperature. The data for a hydrogenated GaAs film (35-2) which did not contain any Si are included in Figure 12(b) for comparison.

These transport results also suggest that the effects of H-evolution at relatively low temperature, clearly evident for a-GaAs:H samples, are not present in the GaAs:Si:H alloys.

VII. CONCLUSIONS ON BINARY ALLOYS

The optical and electrical properties of a-GaAs:H alloys described in earlier sections show all the familiar signatures of H-incorporation, which has led to an increased gap, decreased conductivity and reduced gap state density. Nevertheless, variation of the usual parameters of the sputtering method (T_s , p_H , P_{rf} ...) has not given a material whose photoelectronic properties approach those of the a-Si:H used in solar cells. It seems clear that fine tuning of the parameters of preparation will not bring the material to a useful device state, unless a breakthrough in fundamental understanding is made.

These considerations have led us to review the whole question of binary alloys of the Si family with H. We have noted that alloying C or Ge with a-Si:H has often been reported as deteriorating the device properties rapidly. Therefore, we have asked what specific property of a binary system might be responsible, and this has led us to a detailed study of Ge:Si:H alloys as a prototype system. These alloys have been produced in our sputtering system, and also in the glow discharge system, using various gas mixtures of GeH_4 and SiH_4 . The usual characterization for amorphicity, H-content and Ge/Si content was done. The electrical and optical properties were studied, and also the evolution spectra and the infrared spectra at various stages of anneal.

The results have been written in an article which is attached as Appendix 1, since it gives a rather complete description of the problem and the work done. The conclusion is that, in all binary systems, the H may attach itself preferentially to one atom rather than to the other, and thereby leave the defects on the unfavored atom uncompensated.

It is entirely possible that such preferential attachment is the mechanism at work which is the real degrading agency. A study of the g-values of residual spin centers might provide clues regarding the dangling bond defects. It is also possible that the microstructure is different in the alloys. To our knowledge, studies of these questions have not yet been done.

Figure 12. The temperature dependence of the electrical conductivity: effects of p_H , p_{SiH_4} and isothermal annealing. (a) as-deposited; (b) annealed at 200°C for one hour. $P_{rf} = 140$ watts; $p_{Ar} = 5$ mTorr.

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APPENDIX 1

NEW INSIGHTS ON AMORPHOUS SEMICONDUCTORS FROM STUDIES OF HYDROGENATED a-Ge, a-Si, a-Si_{1-x}Ge_x AND a-GaAs

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1. Introduction

The presence of hydrogen during the process of deposition of thin films of amorphous tetrahedrally-coordinated semiconductors--whether an "accidental" component as in the glow-discharge decomposition of SiH₄ [1] or added deliberately to a sputtering plasma [2]--has become an accepted method of reducing the density of defect-related states in the pseudogap. It has been shown that the density of dangling bonds can be reduced by orders of magnitude and it is further supposed that the density of other types of defect (such as reconstructed weak bonds) may also be reduced. The success of the method has been clearly demonstrated for a-Si [1,2], a-Ge [2] and a-GaAs [3]. Nevertheless, there are quantitative differences between the results for a-Si:H and those for all of the other hydrogenated materials.

The gross effects of incorporation of H are clearly the same. They include (1) decreased electron spin density by several orders of magnitude (2) optical absorption and photoconductivity edges displaced to higher photon energies and often sharpened in slope (3) decreased electrical conductivity at all temperatures, by several orders of magnitude (4) activated electrical transport (5) increased magnitude of photoconductivity and photoluminescence. It does not seem to matter whether the samples are produced by sputtering in an argon-hydrogen plasma or by glow-discharge decomposition of gas mixtures.

A quantitative comparison of the results of hydrogenation of a-Ge and a-Si, presented in Table 1, strongly suggests that the efficacy of H in defect compensation is much greater for Si, despite the fact that deliberately hydrogenated sputtered a-Ge (and, in retrospect, a-Ge:H prepared by glow discharge decomposition of GeH₄) provided convincing evidence of the extent of elimination of the dangling bond defects in unhydrogenated evaporated or sputtered material [1,2].

Group 4-group 4 alloys are known to condense in continuous random networks, so that a-Si_{1-x}Ge_x:H may be regarded as the prototypical hydrogenated binary amorphous semiconductor. All such hydrogenated alloys display similar signatures of dangling bond elimination, but of degree much inferior to a-Si:H. Indeed, it appears that even slight alloying of C or Ge with a-Si:H reduces the effectiveness of hydrogenation. Yet such alloying is naturally thought of as a way of adjusting the energy gap for specific applications, such as solar cells, by analogy with crystalline semiconductors.

Table 1. Comparison of results of hydrogenation of a-Si and a-Ge for several properties. Some of the numbers are approximate. They are taken from various sources, but the differences for the two elements are nonetheless clear

	a-Si	a-Ge	Comment
Lowest reported spin density	10^{16} - 10^{17} cm ⁻³	$>10^{18}$ cm ⁻³	Sputtered
Typical photoconductivity $\Delta\sigma$ at 10^{15} phot/cm ² -s	10^{-6} (1.96 eV) ohm ⁻¹ -cm ⁻¹	5×10^{-8} (1.47 eV) ohm ⁻¹ -cm ⁻¹	Sputtered 200-250°C
Best photoconductivity	2×10^{-5} (1.96 eV) ohm ⁻¹ -cm ⁻¹	10^{-6} (1.47 eV) ohm ⁻¹ -cm ⁻¹	Sputtered 250°C
Photoluminescence	Very efficient	Not reported	
Field effect D.O.S.	$\sim 10^{16}$ cm ⁻³ eV ⁻¹	$>10^{18}$ cm ⁻³ eV ⁻¹	Glow discharge
(ΔG) _{RT} on hydrogenation	$\sim x 10^{-8}$	$\sim x 10^{-4}$	Sputtered
σ_0 in $\sigma = \sigma_0 \exp[-E_\sigma / kT]$	10^3 - 10^4 ohm ⁻¹ cm ⁻¹		Sputtered or Glow discharge
		300 ohm ⁻¹ cm ⁻¹	Sputtered
		10^3 ohm ⁻¹ cm ⁻¹	Glow discharge

Hydrogenated group 3-group 5 compounds, such as a-GaAs:H, also display unmistakable effects of dangling bond elimination, but no photoluminescence, very poor photoconductivity, and no field effect.

In order to try to obtain some insight into the question raised by the differences between a-Si:H and the other materials, we have prepared the hydrogenated elements and alloys of the Si-Ge system [4] and the GaAs system [5] either by sputtering in an argon-hydrogen plasma or by glow discharge decomposition, characterized them structurally and chemically, and measured their principal transport and optical properties. After surveying, in cursory fashion, the general character of the results, I shall focus on a few properties which seem particularly relevant for the establishment of a model to explain the observed poorer efficacy of H-incorporation in materials other than Si.

2. Preparation and Characterization

Our general *modus operandi* is to co-deposit many samples on a variety of substrates under controlled conditions, and after appropriate characterization, to attempt to correlate the measured properties among themselves and with the preparation conditions. Targets of 5" diameter, optical grade crystalline material are r.f. sputtered in an argon-hydrogen plasma. The base turbopump vacuum is between 3 and 5×10^{-7} Torr, with the residual gases established by an attached residual gas analyzer to be H_2O , CO, CO_2 and H_2 . Both target and substrates are plasma-cleaned before deposition is begun. Several substrates of quartz, c-Si, Corning 7059 glass and Al are usually included for any one deposition. The substrate temperatures (nominal, by attached thermocouple) are between 200 and 400°C, the argon partial pressure is usually 5×10^{-3} Torr, and the partial pressure of H may be varied between 0 and 5×10^{-3} Torr. The flow rate of gases is controlled so as to maintain a constant ratio of gas pressures during a run, and the power is set so as to produce a deposition rate of about 1 Å/sec.

The amorphicity is checked by X-ray measurement on selected samples. Densities are checked, again on selected samples, by floating in a liquid of adjustable density. Thicknesses are determined by a Sloan Dektak profile-meter. The gross composition is established by electron microprobe and the profile *versus* depth in the sample of H, O, N, C etc. by secondary ion mass spectroscopy of some of the samples. Scanning and transmission electron microscope studies are carried out in a search for any heterogeneities. Finally, the H-content is estimated from analysis of the infrared vibrational absorption, cross-checked by studies of H-evolution on heating and nuclear reactions with ^{15}N on selected samples.

A large number of property measurements is usually carried out: infrared vibrational absorption between 200 and 3000 cm^{-1} , to establish the nature of the X-H stretching, bending and wagging vibrations; optical absorption edge spectra, to obtain a measure of the energy gap and the gap state density; electrical conductivity as a function of temperature; and steady-state photoconductivity under certain standard illumination conditions. In addition, when other data warrant, we study photoluminescence spectra, as a function of excitation photon energy, excitation intensity, temperature, and applied electric field; thermopower as a function of temperature; photoconductivity spectra and transient photoconductivity; field effect and capacitance-frequency measurements, to obtain an idea of the gap state densities; spin resonance and photo-spin-resonance; and finally, the evolution of H as a function of annealing temperature, which provides information on bonding and diffusion as well as on the H-content.

A simple dc glow discharge system was also used to prepare $a-Si_{1-x}Ge_x:H$ with x between 0 and 1, from different ratio mixtures of SiH_4 and GeH_4 [4]. The total pressure of the combined gases was kept constant in the different preparations with the result that the rate of deposition at constant power varied between 0.1 $\mu m/min$ and 0.5 $\mu m/min$ as x was increased from 0 to 1. The compositional uniformity across the films was checked by electron microprobe to within the instrument sensitivity of 1%, and the actual composition determined to 2%. SIMS measurements showed uniform bulk densities of O less than 0.5% and of C less than 0.1%. These densities are somewhat higher than our usual finding for r.f. sputtered a-Si:H specimens. Sometimes, within 500 Å of the film--c-Si substrate interface of our glow-discharge produced samples, we found an increase of the O and C content. However, it is unlikely

that any properties were substantially altered thereby, since Si-O infrared vibrational absorption was not observed even in 12 μm thick films. TEM and SEM micrographs showed smooth homogeneous regions with no evidence of columnar growth or other heterogeneity, at least down to a scale of 100 $\text{\AA}$.

3. General Properties of $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$

For our glow-discharge preparations of these alloys, we find that many properties change monotonically, but nonlinearly, with x . Figure 1 shows a

Fig.1 Optical absorption edges for a series of $\text{Si}_{1-x}\text{Ge}_x\text{:H}$ films

selection of optical absorption edge spectra and Fig.2 the deduced variation with x of (1) E_{04} and E_{05} , the photon energies at which the absorption coefficient reaches 10^4 and 10^5 cm^{-1} respectively, and (2) E_g , the optical energy gap found by extrapolation of $(\alpha h\nu)^{-1/2}$ versus $h\nu$ to $\alpha=0$, where α is the absorption coefficient and $h\nu$ the photon energy. No corrections for possible alterations with x of the H-content have been applied, since edge spectra at fixed x and variable, known H-content are not available. These results are different from those of CHEVALLIER, WIEDER, ONTON and GUARNIERI [6], who found a linear variation, again without applying any corrections for variation of H-content. As an aside, we note that ANDERSON and SPEAR [7] and later SHIMADA, KATAYAMA and KOMATSUBARA [3], found that the optical gap passed through a maximum with x in $\text{a-Si}_{1-x}\text{C}_x\text{:H}$. For this alloy, however, there are possible complications due to 3-fold and 4-fold coordinated C as well as possible variations in H-content.

Figure 3 shows data on conductivity versus $1/T$ for several alloys. It is seen that there is a wide range in T of activated transport, quite

Fig.2 Deduced energy gaps for a series of $\text{Si}_{1-x}\text{Ge}_x\text{:H}$ films

Fig.3 Conductivity *versus* temperature for a series of $\text{Si}_{1-x}\text{Ge}_x\text{:H}$ films

adequate to define parameters in the equation for the conductivity σ :

$$\sigma = \sigma_0 \exp[-E_\sigma/kT] . \quad (1)$$

Figure 4 displays the deduced variation with composition of E_σ , σ_0 and σ (room-temperature). The activation energy E_σ follows the same general pattern as the optical energy gap: essentially unchanged near 0.85 eV for $x < 0.5$ and then decreasing to 0.5 eV for x approaching 1. The values of σ_0 are in the range commonly found for a-Si:H, and indicate that we are indeed studying transport in the conduction bands of these materials.

Fig.4 Transport parameters deduced from the data of Fig.3

Preliminary data on photoconductivity and photoluminescence are shown in Figs.5 and 6. These show that the relevant magnitudes decrease very rapidly as x is increased from 0, which we believe agrees with the experience of

Fig.5 Relative photoconductivities for a series of $\text{Si}_{1-x}\text{Ge}_x\text{:H}$ films

Fig.6 Relative photoluminescence intensities and peak photon energies for a series of $\text{Si}_{1-x}\text{Ge}_x\text{:H}$ films

other laboratories. The results again suggest, as we intimated in the Introduction, that the addition of Ge increases the gap density-of-states and deteriorates the photoelectronic properties.

There is very little, if anything, in the results to suggest to us *why* the photoelectronic properties are poorer in the alloys and a-Ge. In the next section we shall describe the characterization of the H-content, H-complexes and H-bonding, as revealed by experiments on evolution of H on heating, infrared vibrational absorption spectra, and the changes in the infrared spectra at intermediate stages of anneal. We believe that these experiments *do* suggest the explanation we seek.

4. Selected Properties of $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$

(a) Evolution Spectra

Evolution spectra are taken on films that have been deposited on Al substrates and the Al subsequently dissolved away. An accurately weighed mass of amorphous sample is enclosed in a quartz container of accurately known volume. It is heated so that the temperature increases linearly with time. As gas evolves from the sample, the pressure in the enclosure increases. This is accurately measured with a capacitive manometer. The maximum pressure rise is to about 10^{-1} Torr, which is easily measurable. Two kinds of information are produced. The first, conveniently displayed as dP/dt versus T , tells us at what temperature the H is evolved from the sample. See Fig.7. The second is obtained from the total pressure rise. Knowing this, the volume of the system, and the mass of sample, the atomic percentage of hydrogen in the sample can be deduced [9].

A selection of evolution spectra is shown in Fig.8. We see that, whereas a large fraction of the H evolves from Ge near 150°C , the evolution from Si occurs above 400°C . The spectra for the alloys are intermediate but favor the spectra of the dominant component. Thus, there appears to exist weakly-bonded H in a-Ge:H and Ge-rich $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$ alloys.

The concentration of H found from the total pressure produced is shown in Table 2. The alloys appear to contain more H than the end components.

Fig.7 Typical H-evolution spectra *versus* time or temperature for the Harvard apparatus

Fig.8 Evolution of H from a series of $\text{Si}_{1-x}\text{Ge}_x\text{:H}$ films

Table 2 Characteristics of glow discharge a-Si_{1-x}Ge_x:H alloys

Sample	Composition (Atomic %)			Preferential H Attachment, P
	Ge-content	H-content		
	Microprobe x	Evolution	IR Absorption Wag Mode	
Gegd-2	100	9	2.6	-
Gegd-4*	100	10	5.0	-
SiGegd-1	90	-	3.2	10.5
SiGegd-4	88	-	3.9	13.5
SiGegd-9	82	18	9.4	13.0
SiGegd-12*	70	38	23.0	9.7
SiGegd-8	68	10	9.1	11.6
SiGegd-14	65	13	9.5	10.3
SiGegd-3	55	-	8.0	12.5
SiGegd-2	42	-	11.4	10.4
SiGegd-6	28	-	10.3	8.2
SiGegd-7	26	-	12.0	14.0
SiGegd-13	14	15	9.2	~20
SiGd-4	0	8	10.7	-
SiGd-10*	0	15	11.6	-

*Samples deposited at $T_s = 100^\circ\text{C}$; for all others $T_s = 250^\circ\text{C}$

(b) Infrared Vibrational Absorption Spectra

The infrared spectra of the films were measured in the as-deposited condition and after successive anneals at several temperatures. Representative examples are shown in Fig.9.

The integrated areas under the different modes of vibrational absorption are informative. The integrated area under the wag mode near 600 cm^{-1} may be used to obtain the content of bonded H, by assuming equal matrix elements for absorption by Si-H and Ge-H wag modes, as suggested by the Stuttgart group [10]. These results are also displayed in Table 2; the H-content estimated from absorption is less than that found by evolution, which is itself (because of H diffusion into the quartz of the evolution chamber) a lower bound for the content. This again suggests the existence of weakly-bonded H, especially in a-Ge:H and a-Ge rich alloys.

The absorption in the stretch modes near 2000 cm^{-1} may be deconvoluted to give the relative absorption by Si-H and Ge-H bonds, assuming the matrix elements are not changed by the local environments on alloying. A typical fit is shown in Fig.10. If we now evaluate the quantity:

$$P \equiv \frac{\text{integrated Si-H absorption}}{\text{integrated Ge-H absorption}} \div \frac{\text{Si content} \times \text{Si-H matrix element}}{\text{Ge content} \times \text{Ge-H matrix element}}$$

we get a measure of any preference P of H in bonding to Si rather than to Ge. The relative Si/Ge contents are given by the microprobe analysis. The assumption that the relative matrix elements for absorption by Si-H and Ge-H individual bonds [10], evaluated for the pure elements as 1.9, are not altered by changes in composition, seems a reasonable approximation in view of the near-equal electronegativities of the two elements. [As an aside,

Fig.9 Infrared absorption for a series of $\text{Si}_{1-x}\text{Ge}_x\text{:H}$ films, before and after successive anneals

Fig.10 A typical computer fit (solid line) to the stretching vibrational optical absorption in a $\text{Si}_{1-x}\text{Ge}_x\text{:H}$ alloy film

this assumption may be less reasonable in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys, as discussed by WIEDER, CARDONA and GUARNIERI [11].]

The preference ratio P , given in Table 2, is uniformly close to 10, a result that has great significance for the properties of these and other binaries, as we shall elaborate below.

Next we examine the changes in the spectra on anneal. For pure $a\text{-Si:H}$ prepared at $T_s = 100^\circ\text{C}$ or 250°C , no H is evolved by 250°C , and consistent with this, there is no change in the infrared spectra. The alloys and $a\text{-Ge:H}$ are different. Thus annealing at 150°C for one hour of $a\text{-Ge:H}$ prepared at 100°C evolves a considerable amount of H (see Fig.8), but there is no observed change in the infrared spectra. The same effect is present, although less marked, in the alloys. We conjecture that it is caused by the weakly-bonded H in $a\text{-Ge:H}$ and alloy films, despite the fact that intuition suggests that H should usually induce some signature in infrared vibrational absorption. Our present glow discharge $a\text{-Si:H}$ films do not show this effect, but we have reported, in 1979, that certain sputtering conditions appear to produce weakly-bonded H [12]. Identical conclusions have been reached, in parallel, by DENEUVILLE *et al.*, Grenoble [13] and more recently by ZELLAWA and GERMAIN in Paris [14].

Finally, annealing leads to the observation of Ge-O bands in our glow discharge $a\text{-Ge:H}$, but not in any others. This is taken to reflect a difference in the microstructure of the Ge films from the Si-alloy ones.

Before advancing a tentative explanation of these results, we shall review relevant experience with $a\text{-GaAs:H}$, and $a\text{-Si:H}$ prepared under different sputtering conditions.

5. Selected Properties of $a\text{-GaAs:H}$ Alloys

Our discussion of these alloys can be briefer, since we now wish to focus on certain properties suggested by the work on alloys of $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$. We have, in fact, carried out an even more extensive program of preparation, characterization and property measurement [3,5]. As before, hydrogenation leads to a displacement of the optical absorption edge to higher energies, the occurrence of activated transport, and an improvement in photoconductivity. These results are illustrated in Figs.11-13. There is no photoluminescence or field effect.

The infrared vibrational absorption spectra illustrated in Fig.14 are complex and relatively uninformative about specific modes. This is apparently a result of the occurrence of several Ga-H and As-H modes, occurring in a variety of local environments because of the Ga,As disorder.

The H-evolution spectrum is shown in Fig.15. It shows a very large low temperature peak. Moreover, an anneal which removes the H in this peak does not lead to proportionate changes in the infrared spectrum, suggesting for this material also the presence of weakly-bonded H.

6. Selected Properties of $a\text{-Si:H}$ Prepared at Different Partial Pressures of H

In our investigations of $a\text{-Si:H}$ prepared by sputtering, we have made many samples in the (p_H, T_s) parameter space illustrated in Fig.16. For $T_s = 200^\circ\text{C}$ and $p_H \leq 1$ mTorr, the H-content remains roughly constant at about 20 at.%.

Fig.11 Displacement of the absorption edge of a-GaAs:H to higher photon energies with hydrogenation

Fig.12 Typical conductivity *versus* temperature data for a number of hydrogenated GaAs films

Fig.13 Dependence of the conductivity σ , the photoconductivity $\Delta\sigma$, and the optical gap of a-GaAs:H on the partial pressure of H in the sputtering plasma

Fig.14 Vibrational absorption spectra for pure and hydrogenated a-GaAs before and after anneal

Fig.15 Evolution of H from a-GaAs:H versus temperature

Fig.16 Parameter space for the production of sputtered a-Si:H alloys

However, there appear anomalies in practically all of the properties in Regions marked II-α and II-β; for reasons of space we shall concentrate on the transport results [15].

Figure 17 shows the transport results for Region I, where the H-content is increasing from zero: the conductivity changes regularly, monotonically and comprehensibly from non-activated, Fermi-level hopping for $p_H = 0$ to activated band transport for $p_H = 1$ mTorr. In contrast, the transport results for Region II-β are shown in Fig.18: although the H-content is the same as for $p_H = 1$ mTorr throughout this region, the conductivities are again high and resemble unhydrogenated material in their weak temperature dependence.

It is relevant at this point to describe some properties of samples prepared in Region II-β which concern our present theme. First, there is a relatively greater amount of bending modes at 890 and 840 cm^{-1} , and a relatively greater amount of 2090 cm^{-1} absorption than for samples in Region I. Second, there is a tendency for the evolution spectrum to have more H in a low T evolution peak near 350°C , as is illustrated in Fig.19 [16]. Third, some fraction of the H evolved at this low temperature takes no part in

Fig.17 Conductivity *versus* temperature for a-Si:H samples prepared in Region I of Fig.16

Fig.18 Conductivity *versus* temperature for a-Si:H samples prepared in Region II-B of Fig.16

Fig.19 Evolution of H versus temperature for a-Si:H samples prepared in Regions I and II-B of Fig.16

infrared vibrational absorption, its evolution does not affect the optical absorption edge, and affects in a minor way the photoluminescence spectrum [17].

We have suggested a tentative interpretation of these results in terms of a heterogeneous structure for a-Si:H alloys [15]. The Si nucleates and grows in islands which eventually seek to join together, which leads to essentially a two-phase material of "islands" and connective "tissue" which are different in structure, chemical composition (H-content) and electronic band structure. This model originates in the generally-observed hetero-structure of films deposited from vapors, and the particular observations of microstructure by KNIGHTS and LUJAN [18] on Si-H films produced by glow discharge. In general terms, the transport must be explained on the basis of a percolation theory through two phases with quite different $\sigma(T)$.

7. Integrated Discussion of a-Si_{1-x}Ge_x:H Alloys, a-GaAs:H and a-Si:H of Region II-B

Because of (1) the similarities in the evolution spectra, which favor the release of H at rather low temperature, and (2) the occurrence of weakly-bonded H, as evidenced by the low T evolution and the absence of changes in the infrared spectra, we hypothesize that the structures of 4-4 alloys and a-GaAs resemble those of a-Si:H sputtered at high p_H [4]. In Si-H alloys we suppose that the H-attachment energy is such that Si-H bonds on the surfaces of islands are preferred to reconstructed Si-Si bonds as the film grows. By contrast, we suppose that in a-Ge:H, the H-attachment is weaker so that reconstructed Ge-Ge bonds often win out on the island surfaces. Thus the H may be trapped in the connective tissue. The morphology of Ge, Ge rich alloys and GaAs is such that there is a greater defect density, concentrated in the connective tissue.

Fig.20 Hypothesized microstructure (a), density of electronic states $N(E)$ versus energy (b), band structure versus distance (c), conductivity versus temperature (d), and thermopower versus temperature (e), for the islands (phase 1) and the H-rich connective tissue (phase 2) in a-Si:H films [15]

8. Summary

The more effective removal of pseudogap states in a-Si, by H compensation of defects, over other amorphous semiconductors may now be rationalized. It has several ingredients:

(1) the preference ratio for H-attachment to Si over Ge, a factor of 10, seems to be firmly established, given the argument that the ratio of matrix elements for absorption by Si-H and Ge-H bonds remains constant near the value determined by the Stuttgart group as the composition x of $\text{Si}_{1-x}\text{Ge}_x$ alloys changes. Such preferential attachment is not new in the amorphous semiconductor literature, since the same conclusion was reached earlier, by a somewhat different combination of experiments on a-Si $_{1-x}$ C $_x$:H, by SHIMADA, KATAYAMA and KOMATSUBARA [8]. We believe it to be a general effect possible in all hydrogenated binary systems. It implies that defects connected with one element of a binary may be left uncompensated while H substitutes for the other element, which would provide adequate reason for the poorer photo-electronic properties of all binary alloys with respect to the pure elements. Preferential association of defects with the element unfavored for H-attachment should be detectable through electron spin resonance measurements on lightly hydrogenated binaries.

(2) preferential attachment in a binary does not explain the inferior compensation of defects by H in a-Ge itself. Our hypothesis, which is less firmly based than that concerning preference, nevertheless has the same genesis: it is that the Ge-H bond is less strong with respect to its competitors in a growing film (reconstructed, long Ge-Ge bonds, for example) than is the Si-H bond with respect to its competitors. The end result is a different microstructure which is more highly defected and contains relatively more weakly bonded H.

This model fits the experimental observations on H-evolution and the effect of annealing on infrared absorption spectra rather well.

(3) it is a corollary to our postulates of relatively weak Ge-H bonding that a different compensator might well make the properties of compensated Ge more similar to those for hydrogenated Si. We suggest the distinct possibility that O or F may be suitable. The incorporation of O has the additional advantage that it would promote the joining of growth islands and so reduce the volume of defected connective tissue. Improvement of binaries by this device might remain problematical if preferential attachment occurs for the new compensator; however it is possible that the binding to either element of a binary might still be stronger than the energy of alternative (weak) bonds in the network, so that the latter might still be reduced in density.

We are presently testing these ideas on Ge containing O and F, but have no results we wish to report at this juncture.

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