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SPUTTERED AMORPHOUS SILICON SOLAR CELLS

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PREFACE

This is the second quarterly report of progress on work performed for SERI under Subcontract No. XZ-0-9219. The period covered is from October 22, 1980 to January 22, 1981. The report is divided into the following section:

- Summary
- Experimental evidence for a kinetic model of hydrogen incorporation
- Effect of deep gap states on the hole mobility-lifetime products of undoped hydrogenated α -Si.
- Effect of band gap variations on the diode properties of reactively sputtered α -SiH_x/Pt Schottky barrier structures.
- Device fabrication and performance.
- Appendix A
- Appendix B
- Appendix C

TABLE OF CONTENTS

	<u>PAGE</u>
1.0 SUMMARY	1
2.0 EXPERIMENTAL EVIDENCE FOR A KINETIC MODE OF HYDROGEN INCORPORATION	2
3.0 EFFECTS OF DEEP GAP STATES ON THE HOLE MOBILITY- LIFETIME PRODUCTS OF UNDOPED HYDROGENATED a-Si	3
4.0 EFFECT OF BAND GAP VARIATIONS ON THE DIODE PROPERTIES OF REACTIVELY SPUTTERED a-SiH _x /Pt SCHOTTKY BARRIER STRUCTURES	4
5.0 DEVICE FABRICATION AND PERFORMANCE	5
6.0 APPENDIX A	
7.0 APPENDIX B	
8.0 APPENDIX C	

1.0 SUMMARY

During this quarter we investigated the following areas of the proposed program:

- Through hydrogen content studies we investigated the mechanism of hydrogen incorporation during the film growth. The data are consistent with a kinetic model of hydrogen incorporation.
- The hole mobility-lifetime products have been measured on a-SiH_x/metal Schottky barrier structures with a new method utilizing optical absorption, collection efficiency, and capacitance voltage measurements. By varying the density of states in the middle of the gap by three orders of magnitude, through hydrogen incorporation into the films, we find that the $\mu\tau$ product scales directly with the density of these states whose hole capture cross-section is estimated to be $6 \times 10^{-15} \text{ cm}^2$. The diffusion length of the material with the lowest density of states is about 3000Å.
- The diode properties of reactively sputtered hydrogenated amorphous silicon Schottky barrier structures (a-SiH_x/Pt) have been investigated as a function of hydrogen content. We find a systematic relation between the changes in the optical gap and the changes in the open circuit voltage, the barrier height and the diode quality factor. The data are interpreted in terms of hydrogen modification of the valence band edge and interfacial oxide effects.
- We report the fabrication by the method of sputtering of P-I-N/ITO solar cell structures. Such devices have not been previously reported by any other laboratory and have an engineering efficiency of 3%.

2.0 EXPERIMENTAL EVIDENCE FOR A KINETIC MODEL OF HYDROGEN INCORPORATION

One of the key scientific issues of the program is to understand the mechanism of hydrogen incorporation. In the first quarterly report we proposed, on the basis of density of states and hydrogen content measurements, that the H reacts with the Si at the surface of the substrate and that the reaction is kinetically controlled. The model identify the deposition rate and the hydrogen flux as the important deposition parameter. In this quarter we further tested this model by studying the hydrogen content of films produced with the partial pressure of hydrogen and the deposition rate as the variables. The data were found to be in remarkable agreement with the kinetic model of hydrogen incorporation. In addition we study the hydrogen content as a function of substrate biasing and identify the neutral atomic hydrogen as the important species in the Si and H reactions. The influence of deposition temperature on hydrogen incorporation has also been investigated and the results suggest that, in the deposition range of interest ($T_s = 200-400^\circ\text{C}$), thermal desorption of H from bonding sites during the film growth is negligible. For more details on these results see Appendix A.

3.0 EFFECT OF DEEP GAP STATES ON THE HOLE MOBILITY-LIFETIME PRODUCTS OF UNDOPED HYDROGENATED a-Si

During this quarter we also developed a new method of measuring the diffusion length of the minority carriers. For this purpose we deposited a number of films with the partial pressure of hydrogen as the only variable. Each film was characterized by optical absorption measurements, spectral response of Schottky barrier solar cells and electric field distribution of the Schottky barrier by capacitance/voltage measurements. From the spectral response and optical absorption measurements we determine the collection width, X_c , and from the field distribution measurements we determine the width, X_o , of the space charge layer. The $\mu\tau$ product for holes was calculated by setting the recombination lifetime equal to the time required for carrier to drift the distance X_c . For an exponential depletion region we find

$$\mu\tau = \frac{X_o^2}{V_o} \left[\exp \frac{X_c}{X_o} - 1 \right]$$

Where V_o is the build-in potential. We find that the $(\mu\tau)$ product scales directly with the density of states near midgap. For the films with the lowest density of states ($N = 7 \times 10^{14}/\text{cm}^3 \cdot \text{eV}$) the $\mu\tau$ product has a value of $3 \times 10^{-8} \text{ cm}^2/\text{V}$ or a diffusion length of $2800 \text{ \AA}$. The result suggest that the recombination is controlled by Si dangling bonds. For more details on these results see Appendix B.

4.0 EFFECT OF BAND GAP VARIATIONS ON THE DIODE PROPERTIES OF REACTIVELY SPUTTERED $a\text{-SiH}_x/\text{Pt}$ SCHOTTKY BARRIER STRUCTURES

The diode properties of $a\text{-SiH}_x/\text{Pt}$ Schottky barriers have also been investigated. We find that as the optical gap increases from 1.58 to 1.92 eV, the barrier height increases systematically from 0.85 to 1.26 eV. Correspondingly the diode quality factor decreases from 1.19 to 1.09. These results are accounted for by assuming that the top of the valence band recedes and the valence band tail sharpens with the incorporation of hydrogen. Details on these results are given in Appendix C.

5.0 DEVICE FABRICATION AND PERFORMANCE

The photovoltaic properties of the intrinsic layers are evaluated by fabricating Pt/a-SiH_x Schottky barrier structures. However, the major emphasis for device fabrication has been shifted towards P-I-N/ITO structures. For this purpose we conducted doping studies and developed methods of depositing ITO layers. Details on these studies will be reported in the next report.

The fabricated P-I-N/ITO structures have an efficiency of 3% and are stable devices over a period of time of about 8 months. Typical photovoltaic parameters are $V_{oc} = 0.8$ to 0.9 volts, $I_{sc} = 8$ mA/cm² and FF = 0.45 to 0.53. The I-V characteristics of one such device is shown in Fig. 1. The observed current has been verified by collection efficiency measurements. Fig. 2 shows the collection efficiency of the same device. Indeed, utilizing an AM1 photon flux of 89 mWatt/cm² we find that the current of the device is 7.8 mA/cm² in good agreement with the measured value.

FIGURE 1

SI-266 MO/PIN/ITO#641

AREA 8.55mm²

VOLTS/BIAS ILLUMINATION
100 MW/CM²

AM1 (89 MW/CM²)
 $J_{sc} = 7.8 \text{ mA/CM}^2$

FIGURE 2

6.0 APPENDIX A

TETRAHEDRALLY BONDED AMORPHOUS SEMICONDUCTORS
(Carefree, Arizona, 12-14 March, 1981)

EXPERIMENTAL EVIDENCE FOR A KINETIC MODEL OF
HYDROGEN INCORPORATION INTO SPUTTERED a-Si*

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ABSTRACT

The dependence of hydrogen content, on the partial pressure of hydrogen, substrate bias, deposition rate, and deposition temperature was found to be consistent with a kinetic model of hydrogen incorporation into a-SiH_x films, produced by reactive sputtering in an Ar+H plasma.

INTRODUCTION

Reactively sputtered hydrogenated amorphous Si films were found to have properties similar to those produced by glow discharge decomposition of silane^{1,2}. However, the film growth process appears to be different in these two methods of film formation. For example, there is ample evidence³ that during the glow discharge decomposition of silane the film is formed from Si_xH_y species condensing on the top of the substrate. Spectroscopic studies of sputtering plasmas on the other hand give ambiguous information about the H incorporation mechanism. In one study³ the results suggest that SiH_x molecules are formed in the sputtering plasma. However, the results are not quantitative enough to suggest any correlation between these SiH_x molecules and the film's H content. In the second study⁴ the results^x suggest no silicon-hydrogen gas phase reactions.

In this paper we adopt the view that the reaction of Si with H occurs at the substrate surface. We also suggest that the Si and H reactions are kinetically controlled^{5,6}. In support of this kinetic model of hydrogen incorporation we present hydrogen content data as a function of partial pressure of hydrogen, substrate biasing, deposition rate, and deposition temperature.

EXPERIMENTAL RESULTS-DISCUSSION

The relative amount of bonded hydrogen in the films discussed in this paper was inferred from the integrated intensity under the Si-H vibrational modes. We find no difference in the functional behavior if we plot the integrated intensity under the Si-H stretching or Si-H wagging vibration vs the different deposition parameters. Throughout this paper, therefore, we will use the integrated intensity under the stretching vibration to infer the relative amount of bonded hydrogen.

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The absolute amount of incorporated hydrogen in a few samples has also been measured by the nuclear reaction $^{15}\text{N} + \text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + \gamma$.

Fig. 1 shows that there is a one-to-one relation between the integrated intensity under the stretching vibration and the hydrogen content determined by the ^{15}N reaction. With this calibration we will present the rest of the hydrogen content data in terms of the integrated intensity under the Si-H stretching vibration.

Fig. 1. Correlation between infrared absorption and H content

Fig. 2 shows the relation between the hydrogen content and the partial pressure of hydrogen in the discharge for two series of films. Both series of films were produced at $T_s = 275^\circ\text{C}$ a total pressure of 15 mTorr and power in the discharge of 1.6 watts/cm². The only difference is that during the deposition of one series (solid circles) the substrates were electrically grounded while in the second series (open circles) the substrates were biased to a positive potential.

Fig. 2. Integrated infrared absorption as a function of hydrogen partial pressure.

The relationship shown in Fig. 2 between the H content of the film and the partial pressure of hydrogen in the sputtering plasma can be explained by a kinetic model of the H incorporation as follows⁶. We neglect any gas phase reactions between Si and H, and assume that the H incorporation arises from surface reactions. In the absence of any significant desorption of bonded H, the time dependence of the H coverage on the growing surface is given by,

$$\frac{dN}{dt} = F\theta\sigma (N_{\text{Max}} - N) \quad (1)$$

where N is the number of surface sites occupied by H, N_{Max} is the total number of available sites, F is the flux of hydrogen onto the surface, and θ and σ are respectively the sticking coefficient and capture cross-section of the bonding sites for hydrogen. If the film deposition rate is R (in monolayers/s), then each surface layer has an average time $1/R$ available during which it can capture H atoms.

Taking into account this time limit, we conclude from Eq. (1) that the H content or integrated infrared oscillator strength A_s , obeys the relation,

$$A_s = A_{\text{Max}} \left(1 - e^{-\frac{F\theta\sigma}{R}}\right). \quad (2)$$

Although it is not obvious which species of hydrogen (ion, molecule, atom) is most important in the incorporation process, we expect the flux of all of these species to be proportional to the partial pressure of H in the sputtering gas. To check whether these ideas are reasonable, we can fit the data in Fig. 2 with Eq. (2) and estimate a sticking coefficient θ . From the fit indicated by the dashed line in Fig. 2 we find $\theta = 0.03$ based on the measured deposition rate of 1.1 monolayers/s, the calculated flux F of neutral H_2 molecules onto the surface in a hypothetical neutral gas at the same temperature and pressure and an assumed capture cross-section of 10^{-16} cm^2 . This rather small value for the sticking coefficient (0.03) is reasonable, since only a fraction of the H_2 molecules are decomposed into atomic H in the plasma, and the molecular H is not likely to bond to dangling Si bonds. The close agreement in Fig. 2 between the biased and unbiased substrates demonstrates that the dominant H species in the incorporation process is electrically neutral, probably atomic hydrogen.

According to the kinetic model of the H incorporation process, the hydrogen content should also depend on the film deposition rate. From Eq. (2) we expect the H content to depend on the ratio of the H flux F to the film deposition rate R and not on the two parameters separately. In Fig. 3 we have plotted the integrated IR absorption as a function of P_H/R for three different deposition rates from 1-4 A/sec. Note that the three sets of data fall on the same curve as expected in the kinetic model.

Fig. 3. Integrated infrared absorption as a function of P_H/R .

In the kinetic theory we have neglected thermal desorption of H from bonding sites, and assumed that the H and Si are far from thermodynamic equilibrium. This assumption can be checked by comparing the H content as a function of P_H , for films deposited at different substrate temperatures with other parameters held fixed. The results for two series of films, one deposited at 385°C and one at 225°C are shown in Fig. 4. The first thing to note is that the saturation H content at high P_H is higher for the low temperature films. A plausible explanation of this result is that the growing Si lattice anneals more at 385°C than at 225°C. At the high temperature the Si lattice is likely to be less defective and as a result may have fewer H bonding sites.

Although the data in Fig. 4 at low P_H is incomplete for the high temperature films, there is enough data to conclude that the sticking coefficient θ at high temperature (385°C) is about equal to or larger than the sticking coefficient at 225°C. This observation rules out a thermodynamic equilibrium interpretation of the data. In this interpretation the effective sticking coefficient at a given P_H would be determined by the ratio of the H flux onto the surface to the rate of thermal desorption. The desorption process will involve bond breaking and hence should be thermally activated and strongly temperature dependent. In this case, the apparent sticking coefficient would decrease dramatically from 225 to 385°C, contrary to the experimental results in Fig. 4, where if anything the sticking coefficient goes in the opposite direction. Thus we conclude that the system is far from thermal equilibrium and the kinetic model is appropriate.

Fig. 4. Integrated infrared absorption as a function of hydrogen partial pressures for films produced at $T_s = 225^\circ\text{C}$ (●) and $T_s = 385^\circ\text{C}$ (○).

We thank R. Friedman, M. Hicks and Karen Rogers for sample preparations and measurements.

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7.0 APPENDIX B

EFFECT OF DEEP GAP STATES ON THE HOLE
MOBILITY-LIFETIME PRODUCTS OF
UNDOPED, HYDROGENATED a-Si*

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The hole mobility-lifetime products ($\mu_p\tau_p$) have been measured on a-SiH_x/metal Schottky barrier structures utilizing optical absorption, collection efficiency and capacitance-voltage measurements. By varying the density of states in the middle of the gap by three orders of magnitude, through hydrogen incorporation into the films, we find that the $\mu_p\tau_p$ product scales directly with the density of these states whose hole capture cross-section is estimated to be $6 \times 10^{-15} \text{cm}^2$.

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The transport and recombination properties of electrons in hydrogenated a-Si films produced either by glow discharge decomposition of silane or by reactive sputtering have been investigated through secondary photoconductivity studies (1-3). However, the recombination kinetics of holes, which are the minority carriers in undoped a-SiH_x, have not been investigated yet. In this letter we report a study of mobility-lifetime products of these carriers by a new method, which utilizes optical absorption, photogenerated carrier collection efficiency and capacitance-voltage measurements on a-SiH_x/metal Schottky barrier structures. This method was applied in the determination of the hole mobility-lifetime products ($\mu_p \tau_p$) for a number of films whose densities of deep gap states was reduced in a systematic way through hydrogenation from 5×10^{17} to $7 \times 10^{14} \text{ cm}^{-3} \text{ eV}^{-1}$ (4).

We find that the $\mu_p \tau_p$ products scale directly with the densities of deep lying states and from this dependence we determine for the first time the hole capture cross-section of these states.

The investigated a-SiH_x films were prepared by RF sputtering of a polycrystalline target at a power density of 1.5 Watts/cm^2 , a substrate temperature of 275°C , an Ar pressure of 5mTorr and a variable pressure of hydrogen. The collection efficiency and capacitance-voltage measurements were made on films deposited on glass substrates that have been first coated with a layer of NiCr and 500Å of a-SiH_x doped with phosphorous (3). These layers formed ohmic contact to the undoped a-SiH_x. The Schottky barrier contacts were made to the front surface of the a-SiH_x film by evaporating 100Å Pd or Pt dots having areas 2 mm^2 or 8.5 mm^2 . The films for the optical absorption measurements were deposited on quartz substrates.

The optical densities of the films were measured in a Cary 17 spectrophotometer and the optical absorption coefficient was calculated using an iterative procedure based on Heavens equations (5). The experimental methods of measuring the capacitance-voltage and the collection efficiency of the photogenerated carriers in metal/a-SiH_x Schottky barrier structures have been described elsewhere (6,7).

Fig. 1 shows the optical absorption vs photon energy for some of the investigated films. The optical gap (8) of the investigated films varies from 1.69 and 1.92 eV. The large changes in the optical absorption, seen in Fig. 1, have a large effect on the collection of carrier photogenerated in the Schottky barrier structures because smaller fractions of incident photons are absorbed close to the metal.

Each Schottky barrier structure has been characterized by studying the spectral response of the photogenerated carrier collection efficiency (7). We find that the results can be interpreted in a simple model (7) in which the collection efficiency can be expressed by the relation:

$$Y(\lambda) = 1 - \exp[-\alpha(\lambda)X_c] \quad (1)$$

Where $Y(\lambda)$ is the number of the photogenerated carriers collected per photon entering the a-SiH_x film (internal yield), $\alpha(\lambda)$ is the optical absorption constant and X_c is the collection width. This collection width, which is independent of photon energy, represents the region of the Schottky barrier structure in which the photogenerated carriers are collected with an efficiency equal to, or close to, unity. It reflects directly the contribution of the carrier lifetimes and the electric fields

in the junction, both of which are determined by the gap states in the a-SiH_x films. Utilizing the optical absorption data for each film we determine from Eq. 1 the collection widths, X_c . The results obtained on six films are shown in Fig. 2, where $\ln [1-Y(\lambda)]$ is plotted vs $\alpha(\lambda)$. The slopes of the lines through the experimental points corresponds to X_c . The values X_c of all the investigated films are shown in Fig. 3, where we plot the collection width vs the partial pressure of hydrogen in the discharge. Note that the collection width increases monotonically with hydrogen incorporation into the films from 360Å to 0.95μm.

The capacitance-voltage measurements on the same metal/a-SiH_x Schottky barrier structures have been reported in another paper (4). Some of the results of that study will be used in the interpretation of the present results. The capacitance-voltage measurements have been interpreted in a model which assumes that the density of states close to the middle of the gap is constant. This density of states lead to an exponential depletion region with a characteristic width $X_0 = \sqrt{\epsilon/N_e}$ where ϵ is the dielectric constant and $N(\text{cm}^{-3}\text{eV})$ is the density of states. The values of X_0 for all the investigated films are also shown in Fig. 3.

The measured values of X_c and X_0 can now be used to calculate the $\mu_p\tau_p$ products. It should be emphasized that the values of X_c can be correlated with the values of X_0 only if the collection efficiencies are independent of the level of illumination. In the films reported in this study we found that the spectral dependence of the collection efficiency is the same when studied with only monochromatic light or additionally superimposed bias white light. This observation suggest that the collection

efficiency of the photogenerated carriers is limited by the hole lifetime rather than by the electron lifetime. The electron lifetime was found through photoconductivity studies (1) to depend strongly on light intensity. The transit times of holes across X_c is given by:

$$\tau_r = \int_0^{X_c} \frac{dx}{V_p(x)} = \int_0^{X_c} \frac{dx}{\mu_p E(x)} \quad (3)$$

where $V_p(x) = \mu_p E(x)$ is the velocity at x , μ_p is the hole mobility and $E(x)$ is the electric field. The spatial distribution of the electric field, according to the model used to interpret the capacitance-voltage measurements (4), can be expressed in the form:

$$E(x) = \frac{V_0}{X_0} \exp\left(-\frac{x}{X_0}\right) \quad (4)$$

where x is the distance from the metal contact, and V_0 is the built-in potential. From Eqs (3) and (4) we find:

$$\tau_r = \frac{X_0}{\mu_p V_0} \left[\exp \frac{X_c}{X_0} - 1 \right] \quad (5)$$

In order to collect all the carriers photogenerated in X_c it is necessary for their transit times to be greater or equal to the hole recombination lifetimes, τ_p . This leads to $\mu_p \tau_p$ product given by the expression:

$$\mu_p \tau_p = \frac{X_0^2}{V_0} \left[\exp \frac{X_c}{X_0} - 1 \right] \quad (6)$$

Utilizing Eq. (6) and the measured values of X_c and X_0 we calculated the $\mu_p \tau_p$ products for all the investigated films. Fig. 4 shows the $\mu_p \tau_p$ products vs the density of states in the middle of the

gap (4). Note that the $\mu_p \tau_p$ products scale directly with the density of states, implying that the hole recombination proceeds through these deep gap states. The hole capture cross-section, S_p , of these states can be evaluated from $\tau_p = 1/S_p N v$. Using a value for the hole microscopic mobility of $\mu_p = 1 \text{ cm}^2/\text{V}\cdot\text{Sec}$ (9) and assuming that the thermal velocity is $v = 10^7 \text{ cm/sec}$ we find $S_p = 6 \times 10^{-15} \text{ cm}^2$. Such a value for the capture cross-section suggests that the deep gap states in a-SiH_x are neutral recombination centers (10). This agrees with the earlier finding (4) that these states are Si dangling bonds.

In conclusion, we have used optical absorption, photogenerated carrier collection efficiency and capacitance-voltage measurements to determine the lifetimes of holes in undoped a-SiH_x films. By systematically varying the amount of hydrogen in the films, we find that the hole lifetime scales directly with the densities of states in the middle of the gap. These states, which have been associated with Si dangling bonds, are found to have a hole capture cross-section of $6 \times 10^{-15} \text{ cm}^2$.

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FIGURE CAPTIONS

- Fig. 1 The optical absorption constant vs photon energy for some of the investigated films.
- Fig. 2 Determination of collection width X_c from $\ln[1-Y(\lambda)]$ vs $\alpha(\lambda)$ plots.
- Fig. 3 X_c and X_0 vs the partial pressure of hydrogen in the discharge for the investigated samples.
- Fig. 4 The $\mu_p\tau_p$ products vs the inverse of the density of states in the middle of the gap for the investigated samples.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

8.0 APPENDIX C

EFFECT OF HYDROGEN ON THE DIODE PROPERTIES
OF REACTIVELY SPUTTERED AMORPHOUS SILICON
SCHOTTKY BARRIER STRUCTURES*

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ABSTRACT

The diode properties of reactively sputtered hydrogenated amorphous silicon schottky barrier structures ($a\text{-SiH}_x/\text{Pt}$) have been investigated. We find a systematic relation between the changes in the optical gap, induced by the hydrogen incorporation, and the corresponding changes in the open circuit voltage, the barrier height and the diode quality factor. These results are accounted for by assuming that hydrogen incorporation into the amorphous silicon network removes states from the top of the valence band and sharpens the valence band tail. Interfacial oxide layers play a significant role in the low hydrogen content, low band gap regime.

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The diode properties of hydrogenated amorphous silicon produced by glow discharge decomposition of silane have been extensively investigated¹. These studies have shown that intimate metal/a-SiH_x Schottky barrier structures are near ideal diodes. The current voltage relation under forward bias was found to follow the form:

$$J = J_0 [\exp(qV/nKT)-1] \quad (1)$$

where the saturation current density, J_0 , was found to be consistent with the diffusion theory of metal-semiconductor rectification. Thus, J_0 is given by²:

$$J_0 = q\mu N_c E_s \exp(-\phi/KT) \quad (2)$$

where μ is the electron mobility, E_s is the surface electric field in the semiconductor, N_c is the effective density of states in the conduction band, and ϕ is the barrier height. The value of J_0 for the Pt barriers, extracted either from the dark I-V curves or from the photocurrent-photovoltage measurements, was found to be 1×10^{-12} A/cm². This, in conjunction with Eq.(2) leads¹ to a value for the Pt barrier height of $\phi=1.1$ eV. Such a value has also recently been confirmed by internal photo-emission studies³. The diode properties of hydrogenated amorphous silicon produced by reactive sputtering have been investigated by Thompson et al⁴. These authors have shown that these diodes show various characteristics depending on the defect structure of the a-SiH_x film.

In this letter we report for the first time the effect of hydrogen incorporation on the diode properties of reactively sputtered hydrogenated amorphous silicon films. We find that the band gap of the material, which we determine optically, increases with the amount of incorporated hydrogen. The open circuit voltage and the barrier height were found to increase

systematically with the band gap. The data are interpreted in terms of hydrogen modification of the valence band edge and tail and interfacial oxide effects.

The $a\text{-SiH}_x$ films were prepared by RF sputtering of a polycrystalline target at a power density of 2W/cm^2 , a substrate temperature of 275°C , an Ar pressure of 5mTorr and partial pressure of hydrogen varying from 0.3 to 1.5mTorr. The hydrogen content of the deposited films was found to vary from 8 to 23 at.%. The Schottky barrier structures were fabricated on stainless steel substrates, which were first coated with $500\text{\AA}$ of $n^+ a\text{-SiH}_x$ ⁵ to form an ohmic contact with the undoped amorphous silicon whose thickness is approximately $1.5\mu\text{m}$. A Schottky barrier contact was made to the front surface of the $a\text{-SiH}_x$ film by depositing $50\text{\AA}$ of platinum either 2mm^2 or 8.5mm^2 in area. The Pt transmission was about 50%. Care was taken to deposit the metal on freshly prepared $a\text{-SiH}_x$ films. The films for the optical absorption measurements were deposited on quartz substrates.

The optical densities of the films were measured in a Cary 17 Spectrophotometer, and the optical absorption coefficient was calculated using an iterative procedure based on Heavens equations⁶. The diode properties were investigated by studying the photocurrent-photovoltage characteristics. The dark I-V characteristics were not extensive enough because of series resistance limitation effects. The diodes were illuminated with an ENH lamp, whose full light intensity was adjusted to be 100mW/cm^2 . Calibrated neutral density filters were used to alter the light intensity.

Fig. 1 shows the relation between the open circuit voltage, V_{oc} , generated by the Schottky barrier structures under illumination with 100mW/cm^2 from the ENH lamp, and the optical gaps of the films. These results show a systematic increase of V_{oc} with the degree of hydrogenation. The optical

gaps, E_g , of the films were defined by the relation $(ah\nu)^{1/2} \sim (h\nu - E_g)^{1/2}$.

To understand the origin of the voltage generation and its relation to the optical gap we determined the barrier heights of the investigated diodes. Fig. 2 shows the photocurrent-photovoltage characteristics of representative diodes. With the exception of the diode with the largest band gap, the I-V curves can be fitted to Eq. 1 leading to the indicated diode quality factors. The largest band gap sample exhibits two distinct slopes. The low voltage slope may be due to shunting or may indicate the onset of a different mechanism. The trend of these data indicate that the diodes approach the ideal behavior with the degree of hydrogenation. Utilizing Eq. 2 and making reasonable assumptions¹ about the values of the pre-exponential factor we were able to calculate the barrier height for the different diodes from the resulting J_0 values. For the large band gap material we used the high voltage branch.

Fig. 3 shows the relation between the barrier height and the optical gap of the material. The barrier height from two of the samples was also determined from the temperature dependence of J_0 . J_0 vs $1/T$ for these samples is shown in Fig. 4. The slopes of these lines, according to Eq. 2 are equal to the barrier height. These values are in good agreement with those determined from the light I-V curves and suggests small effects due to changes in the preexponential term. Note that the barrier height varies continuously with the degree of hydrogenation from 0.85 to 1.25 eV.

These experimental results can now be accounted for in the following way. The barrier height is the energy difference between the platinum electrode and the bottom of the conduction band. A plausible interpretation of the data is that the increase of the optical gap is due to the downward movement of the valance band and corresponding downward movement of the energy at which the platinum electrode contacts the material. In such an

interpretation the platinum level appears to be pinned in the valence band tail. An alternative interpretation in which the valence band and the platinum level remain fixed while the conduction band moves upwards with the degree of hydrogenation appears to be inconsistent with experimental evidence⁸ and theoretical calculations⁹.

The increase in barrier height with band gap seen in Fig. 2 is the result of a complex interplay of mechanisms. Firstly, the systematic decrease of the diode quality factor, n , with increasing band gap (Fig. 1) is suggestive of the presence of an operable oxide layer on the surface. McGill and Wilson¹⁰ demonstrated an increase in both n and ϕ as they increased the thickness of a TiO_x oxide layer on a-SiH_x . Their results were interpreted from Card and Rhoderic's analysis of crystalline MIS structures according to the equation¹¹:

$$n = 1 + \frac{\delta}{\epsilon_I \epsilon_0} \left(\frac{\epsilon_0 \epsilon_s}{W} + e D_s \right) \quad (3)$$

where ϵ_I and ϵ_s are the dielectric constants of the insulator and semiconductor respectively, δ is the thickness of the oxide layer, W is the depletion width and D_s is the interface state density. The observed decrease in n with increasing band gap can thus be interpreted in terms of a diminishing oxide layer with increasing band gap which is consistent with other evidence¹².

The dependence of ϕ on band gap is related to the above considerations in the following way. To a first approximation one might expect the barrier height to track the band gap on a one-to-one basis. As seen in Fig. 3, however, the dependence is smoothly increasing from less than one-to-one at low band gaps to greater than one-to-one at higher band gaps. We believe that the initially sluggish behavior in the low band gap region is due to control of the barrier height by a significant oxide layer. That is,

the barrier heights for the low band gap region are incrementally higher due to the oxide layer. (McGill and Wilson realized a 170 mv increase in going from an intimate contact to a 1.3nm thick oxide.) The accelerating dependence at higher band gaps is due to a third mechanism. In this region the oxide effect should be neutralized and one might again expect one-to-one tracking. We believe the observed additional incremental increase in ϕ with gap over the expected one-to-one relationship to be due to sharpening of the valance band tail. That is, as hydrogen is added, in addition to the shift in the valence band edge as discussed above, there is an accompanying reduction in tail states such that the Pt electrode contacts the $a\text{-SiH}_x$ at an incrementally lower energy within the gap. Thus, as hydrogen content is increased, the $a\text{-SiH}_x$ films start approaching more classical and ideal behavior with diode quality factors and barrier heights representative of oxide free surfaces and sharp band edges.

In summary, the diode properties of $a\text{-SiH}_x/\text{Pt}$ Schottky barriers have been investigated. The diodes approach ideality with the degree of hydrogenation. The barrier height increases systematically with the optical gap due to a complex interplay of mechanisms. The data are consistent with downward movement of the valence band and sharpening of the valence band tail with the degree of hydrogenation. At low hydrogen content oxide layers play a significant role in determining the diode properties.

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12. Although all films were grown under the same system leak rate, evidence of Si-O vibrations, from infrared vibrational data, occurs only for the low hydrogen content films. This suggests that the films oxidize more readily when they are not fully hydrogenated. We speculate that the oxidation rate of the free surface would also be higher for films with low hydrogen content.

FIGURE CAPTIONS

- Fig. 1 Open circuit voltage under ENH illumination verses band gap for $a\text{-SiH}_x/\text{Pt}$ Schottky barriers.
- Fig. 2 Short circuit current verses open circuit voltage for several of the devices of Fig. 1.
- Fig. 3 Barrier height verses band gap from: $\bullet$ - J_0 values assuming a preexponential ($q\mu N_c E_s$) of $3 \times 10^6 \text{ A/cm}^2$; $\square$ - J_0 verses temperature.
- Fig. 4 J_0 as a function of temperature for samples 246 and 248.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4