Research on the Stability, Electronic Properties, and Structure of a-Si:H and Its Alloys

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EXECUTIVE SUMMARY

OBJECTIVES

The objective of this research program is to obtain a comprehensive understanding of the structure and electronic properties of a-Si:H as they apply to solar cells. The main emphasis is on the phenomena of metastability and thermal equilibrium, in which the density of electronic states depend on the electronic and thermal history of the material. Metastability effects are a major problems with solar cells and with other electronic devices. Our studies provide an understanding of the complex interaction between the electronic states and the atomic structure which cause these effects.

APPROACH

Our approach is to study metastability in several different ways so that the combined results give a broad picture of the physical mechanisms. Our previous research has led us to conclude that defect creation is induced by hydrogen motion. We therefore study hydrogen diffusion, the bonding of hydrogen to silicon and explore growth of a-Si:H in a remote hydrogen plasma. We also study defect creation by a forward bias current in p-i-n devices, and thermally induced metastability in doped a-Si:H, to contrast with light induced defects. Electrical transport is studied to provide the understanding which is essential for the interpretation of many measurements of metastability. The transport studies focus on the forward and reverse characteristics of p-i-n diodes and high field transport at low temperature.

SUMMARY OF ACCOMPLISHMENTS

- The first observations were made of light enhancement and field suppression of the hydrogen diffusion in a-Si:H. These results give further strong evidence for the involvement of hydrogen in the metastability. Detailed studies were also made of how the hydrogen diffusion depends on the hydrogen concentration, providing experimental information about the hydrogen density of states distribution and the hydrogen reactions.
- Theoretical studies were made of the hydrogen density of states distribution and its relation to the defect metastability. These studies include calculations of the H

binding energy to weak Si-Si bonds, and how alloys modify the hydrogen density of states .

- A reduced density of light induced defect is observed in a-Si:H deposited in a remote hydrogen plasma (RHP) reactor with a deposition temperature of 400°C. Improved stability is also demonstrated in doped samples under the same deposition conditions. Characterization of the 400°C RHP films showed a low equilibrium defect density, high conductivity of doped films and a internal stress which peaked at the optimum growth temperature.
- The kinetics of metastable defect creation using forward bias in a p-i-n diode to induce defects were studied and compared to light induced defect creation in the same devices. The first observation was made of defect recovery under forward bias. Transient forward bias characteristics of p-i-n cells were explained in terms of the potential barriers at the contacts and it was shown that the time dependence is sensitive to metastable defects.
- Studies were made of transport at high electric field and low temperature. We find that the drift mobility and d.c. conductivity increase as the 10-15th power of the field and is due to field enhanced hopping in band tail states.
- Detailed studies were made of the kinetics of dopant metastability in n-type and p-type a-Si:H. Differences in the stretched exponential relaxation rates for dopant activation and passivation were observed and explained in terms of the atomic structural changes.

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Stability, electronic properties and structure of a-Si:H and its alloys

1. METASTABLE DEFECTS IN A-SI:H

A. Metastability in remote plasma deposited a-Si:H

Nearly all of the studies on stability have been conducted on material deposited in an rf glow-discharge (GD) deposition system. Our work demonstrates that the stability of a-Si:H thin films is improved by deposition at high T_D 's (e.g., 400°C) in a remote hydrogen plasma (RHP) deposition reactor. It is proposed that the improvement is a consequence of two effects: (1) the use of hydrogen dilution during deposition to maintain the hydrogen concentration in the film near 10 at. % even at 400°C and (2) the possibility that at high T_D 's the hydrogen is more stably incorporated in the random network and/or that the density of weak Si-Si bonds is smaller.

In comparison with a GD system, the principal features of an RHP reactor are the elimination of charged-particle bombardment, and isolation of a single primary gas-phase reaction (i.e., $H + SiH_4 \rightarrow H_2 + SiH_3$) to generate gas-phase precursors for film deposition. The RHP deposition conditions were as follows: 200 sccm H_2 , 10 sccm SiH_4 , microwave power of 400 W (2.45 GHz), and a chamber pressure of 0.5 Torr.

The density of gap states in undoped RHP-deposited a-Si:H was probed with optical absorption spectra from photothermal deflection spectroscopy (PDS) for films with different deposition temperatures. The spectra reveal the following: (1) the midgap defect density decreases with increasing T_D , being lowest at 400°C, the highest T_D in this study, (2) the Urbach edge is identical within experimental accuracy over the entire range of T_D 's, and (3) for $T_D = 400^\circ\text{C}$ the midgap absorption is less than or comparable to that for optimized (250°C) GD films. Both PDS and the constant photocurrent technique yielded a slope of ~ 50 meV for the Urbach edge in

FIG. 1. Temperature dependence of the dark dc conductivity for *n*-type a-Si:H after rapid quenching from different temperatures T_Q . Also shown is the curve for a slow cooling and the equilibration temperature T_E for each of the quenched curves.

the 400°C material, which indicates that the degree of the silicon network disorder is as low as that in the 250°C GD material.

The temperature dependence of the dark dc conductivity for an *n*-type a-Si:H film is shown in Fig. 1. The conductivity is shown after rapid (10°C/s) or slow (0.05°C/s) quenching from different temperatures. Also shown is the equilibration temperature T_E for each of the quenched curves. Of particular importance is the observation that for rapid quenching, T_E is greater than the value of 130°C that has been commonly reported⁸ for optimized *n*-type GD films. This feature suggests an increase in electronic stability. If T_E is related to the migration of hydrogen and its interaction with donor dopants, as has been reported, this feature further suggests that the change involves an increase in the thermal stability of hydrogen.

The apparent increase in electronic stability is directly substantiated in Fig. 2 with an Arrhenius analysis of the relaxation time of the dark dc conductivity in *n*-type

FIG. 2. Arrhenius analysis of the relaxation time of the dark dc conductivity in *n*-type a-Si:H deposited at 400°C in a RHP reactor. Also shown are results for a similarly doped film deposited in an rf glow-discharge reactor at 230°C. Both films were initially rapidly quenched from 280°C to room temperature.

films that have nearly the same Fermi level. For direct comparison results are also shown for a similarly doped film deposited in a GD reactor at 230°C; the activation energy of the conductivity above T_E was 0.28 eV, which is close to that for the RHP film (see Fig. 1). The measurement involved first rapidly quenching from 280°C to room temperature, then ramping the temperature to a pre-selected fixed value, and finally monitoring the conductivity over time. The transients displayed the normal stretched exponential time dependence. The results reveal that the relaxation time at any given temperature is longer and the activation energy for the relaxation process is larger for the 400°C/RHP film.

Since hydrogen migration has also been implicated in the Staebler-Wronski effect, the kinetics of light-induced defect generation were investigated. In Fig. 3 is shown the dependence of the defect density in undoped a-Si:H on illumination time. To permit a direct comparison, specimens from both RHP and GD reactors were

FIG. 3. Dependence of the density of light-induced defects on illumination time. The specimens were deposited in either a remote hydrogen plasma (RHP) reactor or an rf glow-discharge (GD) system.

simultaneously illuminated with filtered white light at a substrate temperature of 350 K, and the defect densities were determined by the constant photocurrent technique. The results reveal the following: (1) the pre-illumination defect density N_s is lowest for the 400°C/RHP film, (2) the rate of generation of light-induced defects (i.e., slope of $\log N_s$ versus $\log t$) is comparable for the RHP and GD films, and (3) the 400°C/RHP film saturates at a lower defect density than the simultaneously illuminated GD films. These results were further substantiated with measurements of light-induced spin density by electron spin resonance after long illumination times at room temperature. Although the difference in the saturated defect density is small (a factor of ~ 2), it is a reproducible result that correlates with the different deposition conditions.

The results identify an improved thermal stability for a-Si:H films deposited at 400°C in an RHP reactor, as compared to optimized GD films. Further, the

improvement appears to relate to a quantitative change in the migration kinetics of hydrogen. The improvement in thermal stability must ultimately relate to some structural change in the random network of the silicon-hydrogen alloy. One possibility is that the hydrogen is more stably incorporated in the random network during deposition at the higher T_D 's. In this case higher temperatures would be required to overcome the greater binding energies of more stable hydrogen complexes. This in turn would yield a greater dissociation energy, even if the activation energy for hydrogen diffusion were the same as in GD material. Another, not necessarily mutually exclusive, possibility is that the density of weak Si-Si bonds is smaller in the high T_D material. This could account, for example, for the lower saturated density of light-induced defects in Fig. 3. While in principle a decrease in the band tail density should be manifest in the Urbach slope, the requisite decrease in slope is expected to be less than the measurement accuracy. Finally, in addition to the need for further evaluation of possible mechanisms, consideration should be given to the possibility that the unique conditions that produce the improved stability in a remote hydrogen plasma reactor can be realized, at least approximately, in a glow-discharge system.

B. Current-induced defect creation

Metastable defects in a-Si:H are induced by many processes, including illumination, bias and current flow with the common feature is that defects are created by the presence of excess carriers. We have studied defect creation by a forward bias current in p-i-n devices. The forward bias current increases exponentially reaching about 1 A/cm² when a few volts are applied in a device of thickness 1 μ m. In contrast, the reverse bias current is typically 10⁻¹¹-10⁻⁹ A/cm². When contact injection of carriers is negligible, the reverse current arises from thermal generation out of deep gap states within the i-layer and is given by,

$$J_{th} = \zeta(V) e N(E_{FD}) \Omega kT \omega_0 \exp[-(E_C - E_{FD})/kT] \quad (1)$$

where $N(E_{FD})$ is the density of gap states at the trap quasi-Fermi energy E_{FD} , E_C is the energy of the conduction band mobility edge, $\zeta(V)$ describes the weak voltage dependence of the current, and Ω is the sample volume. Under conditions of deep depletion, E_{FD} is near the middle of the band gap at the energy where the rates of electron and hole excitation are equal. The reverse current is proportional to $N(E_{FD})$ and is therefore a measure of the density of deep defect states. Our previous measurements have shown that the thermal generation current in annealed samples

is consistent with the measured depletion charge and with a defect density of about $3 \times 10^{15} \text{ cm}^{-3}$. The reverse current increases after light soaking with the same kinetics as observed in ESR measurements, confirming that this is a reliable technique for measuring metastable defect creation.

The samples used in this study were p-i-n structure of thickness $1 \mu\text{m}$, in which thermal generation dominates the reverse current. Defects were induced by passing a forward current through the device for different time periods. After each period the reverse current was measured from 0 to 5V. The defect density was obtained from the current at 2V, using the calibration obtained in previous studies.

Fig. 4 shows the defect creation kinetics at different values of the forward current from 10^{-3} to 1 A/cm^2 , and for times up to 1000 minutes. The forward J-V

FIG. 4. Time dependence of the current-induced and light-induced defect density for different generation conditions. The left vertical axis is the reverse current at 2V, and the right axis is the estimated defect density.

characteristics changed during the current soaking (see below), and the applied voltage was altered periodically to keep the current constant. The defect density

increases with time and eventually reaches a steady state at sufficiently long times. The steady state value increases by about a factor 2 for each order of magnitude increase in the current. In the intermediate time range, the creation kinetics are described approximately by the time dependence,

$$ND(t) \approx \text{const } t^{1/2} \quad (2)$$

as compared to the $t^{1/3}$ dependence found for light-induced defects. One possible origin for the difference in rates is that the current is held constant in this experiment, whereas the excess carrier density decreases with time in the light soaking measurement, as defects are created.

The induced defect density is similar to that found for light soaking, with saturation values of about 10^{17} cm^{-3} . Furthermore the current-induced defects are removed by annealing at similar temperatures of 150-200 °C.

The temperature dependence of the defect creation is rather weak, and corresponds to a creation rate with an activation energy of about 0.2 eV. Light induced defect creation has a similarly low activation energy. In contrast, defects created by bias have an activation energy of more than 1 eV. We attribute the low activation energy to a defect creation mechanism involving the recombination of electrons and holes which can provide most of the energy needed to overcome the barrier to defect creation. In measurements made under accumulation bias, there are no minority carriers and therefore no recombination. Instead, a large thermal energy is needed for defect creation.

The steady state defect density at long inducing time is reduced at elevated temperature. There is only a small change between 295 and 340K, but a larger change at 380K. The reduction of the saturation level is explained by thermal annealing and is qualitatively similar to measurements on light-induced defects.⁴

A surprising new result of these measurements is that defect recovery is also induced by a forward current, as is shown in Fig. 5. A defect density above 10^{17} cm^{-3} was first created by passing a high forward current for an extended time. The current was then reduced by a factor of about 100 and the defect density was measured after progressively increasing times. During the measurements the defect density measured by the thermal generation current decreased by a factor 2-3 (curves A and B), and approached a value equal to the steady state defect density generated from the annealed state by this current (curve D). A much smaller reduction occurred when no current was passed after the initial defect creation

FIG. 5. Measurement of the current-induced defect recovery after defect creation at a current of $1\text{A}/\text{cm}^2$ for about 1 hour. Curves A and B are for constant voltage (1.7V) and constant current ($5\text{mA}/\text{cm}^2$) respectively; curve C shows the small recovery in the absence of a forward current; and curve D is the defect creation rate for a current of $5\text{mA}/\text{cm}^2$.

(curve C), showing that the defect recovery was indeed induced by the current. We conclude that at room temperature, the steady state defect density is a balance between induced defect creation and induced recovery. Hence we expect little temperature dependence to the saturation level near room temperature, and an increasing temperature dependence as the thermal annealing mechanism becomes more important.

Figure 6 shows the measured and calculated forward bias J-V characteristics of these devices. The annealed samples exhibit an exponential dependence of current on voltage up to about 1V ,

$$J(V) = J_0 \exp[eV/nkT] \quad (3)$$

FIG. 6. (a) Measured forward J-V curves for the annealed state and at various stages of current soaking; (b) numerical calculations of the J-V curves for defect densities corresponding to the measured conditions.

with an ideality factor, n , of 1.5. The prefactor J_0 is $\sim 2 \times 10^{-12}$ A/cm² and is consistent with the reverse thermal generation current of about 10⁻¹¹ A/cm². Figure 6 also shows the effect of defect creation on the J-V curves. As the defect density increases there is first a proportional increase in the current at low voltage ($V < 0.4$ Volts), with little change at higher voltage. Induced defect densities above about 5×10^{16} cm⁻³ cause a strong reduction in the forward current above 0.4 V, such that when the defect density reaches 2×10^{17} cm⁻³ the current at 1V has decreased by more than a factor 1000. At higher voltages the defects have a smaller effect, and the maximum current drop is only a factor 2 at 6V.

The changes in the forward current are reversible either by thermal annealing or by current-induced recovery. For example, the forward current at 1.7 V increased by 35 times during the recovery measurement illustrated in Fig. 5.

Figure 6 shows that numerical calculation of the J-V curves agree well with the measured values. In the annealed state, the calculations reproduce the forward J-V

curves almost exactly. The prefactor is close to the measured value and the ideality factor is 1.4 rather than the measured 1.5, which results in a slightly higher current at larger voltages than is measured. The changes that occur with an increase in defect density are qualitatively similar to the measurements. As the defect density increases, the low-voltage current at first increases and when the defect density is high, the high voltage current decreases rapidly. Comparison of Figs 6a and 6b show that the experimental behaviour is well reproduced although the detailed shape is less accurately obtained. The calculations show that the enhanced low-voltage current is due to thermal generation from the larger density of states, while the decrease in current at high voltage is due to faster recombination in the i-layer.

1. HYDROGEN DIFFUSION AND METASTABILITY

Hydrogen diffuses relatively rapidly through the amorphous network at low temperatures, and modifications of the hydrogen bonding configuration due to hydrogen migration have been proposed as a mechanism for metastable defect generation in a-Si:H. A correlation between hydrogen diffusion and defect generation has so far only been demonstrated indirectly, by comparing the kinetics of defect generation and annealing with that expected from hydrogen diffusion. We present the first experimental evidence of light-induced hydrogen motion in undoped a-Si:H, obtained from diffusion experiments under strong illumination. The results establish a direct connection between hydrogen motion and light-induced defect generation in a-Si:H.

A. Light-enhanced H diffusion

Light-enhanced hydrogen diffusion was investigated using secondary ion mass spectroscopy (SIMS) to measure H and D concentration profiles of deuterated films. Two techniques of deuteration were used:

A) Multilayer films were grown with a buried deuterated layer. The a-Si:H/a-Si:H:D/a-Si:H structures have layer thicknesses of 100nm, 200nm, and 500 nm, respectively (from the top surface). The bottom a-Si:H film was grown by glow discharge decomposition of pure silane at 230°C. The two capping layers were deposited at a lower temperature (130 °C) to reduce deuterium diffusion during growth, and deuterium incorporation was achieved by diluting silane with a 20% volume fraction of deuterium.

B) Single a-Si:H films were exposed to monoatomic deuterium in a remote microwave plasma system. In this case, the specimen was optically isolated from the deuterium plasma and illumination was provided by an argon laser with wavelength 514.5 nm.

Light-enhanced deuterium diffusion in the multilayer structures is illustrated in Figs. 7a to 7c, by comparing deuterium concentration profiles annealed in the dark (thin lines) and under illumination (thick lines). In the diffusion experiments, the

FIG. 7. (a)-(c) Concentration profiles for diffusion from a deuterated layer in the dark (thin lines) and under an illumination intensity of 17 ± 2 W/cm² (thick lines). The diffusion temperature and time are indicated in each case, and the vertical line indicates the interface between the a-Si:H:D and the a-Si:H layers. In (d) the corresponding profiles for diffusion from a deuterium plasma are displayed. The illumination intensity in this case was 20 ± 2 W/cm².

multilayers were irradiated with water-filtered light from a xenon arc-lamp which has a flat spectral irradiance from 350 nm to 800nm. An illumination intensity of 17 ± 2 W/cm² was used and the annealing times and temperatures are indicated in

each case. The deuterium concentration drops from $7 \times 10^{19} \text{ cm}^{-3}$ in the a-Si:H:D layer, corresponding to an atomic concentration of 1.5% relative to the silicon atoms, to the natural deuterium abundance of $6 \times 10^{17} \text{ cm}^{-3}$ in the a-Si:H layer. Diffusion in the dark is undetectable at 200°C and below. Diffusion is strongly enhanced under illumination, as can be seen in the SIMS profiles at temperatures above $\sim 175^\circ\text{C}$. Diffusion in the dark and under illumination are thermally activated and the largest difference occurs at 250 °C, for the illumination intensity used.

The deuterium concentration profiles in the a-Si:H layers fit to a complementary error function, $\text{erfc}(x/2\sqrt{Dt})$, where x is the depth in the layer, and D and t are, respectively, the diffusion coefficient and the time. Diffusion coefficients are plotted as a function of the inverse temperature in Fig. 8 (solid and open dots). In

FIG. 8. Temperature dependence of the deuterium diffusion coefficient in the dark (solid symbols) and under illumination (open symbols) for diffusion from a deuterated layer (dots) and from a deuterium plasma (squares).

the temperature range from 200 to 350 °C, Illumination reduces the activation energy from about 1.4 eV to 0.9 ± 0.1 eV. At 250°C ($1000/T=1.9$) the diffusion

coefficient under illumination is enhanced by an order of magnitude, and the enhancement is even larger for lower temperatures.

The dark diffusion coefficient of compensated and phosphorus doped samples is approximately a factor of 10 larger than undoped material, and the boron doped material is a factor of 100 larger. Under illumination, small changes were observed in the concentration profiles of doped samples. The diffusion coefficient increased by less than a factor of 2, which is much less than the increase in undoped samples.

The light enhanced diffusion coefficient is proportional to the illumination intensity, for measurements performed at 250°C. The photoconductivity was

FIG. 9. Photoconductivity, σ_{ph} , versus illumination intensity, F , for different temperatures. The exponent γ in the relationship: $\sigma_{ph} \propto F^\gamma$ is indicated in each case.

measured under the illumination conditions of the diffusion experiments and is shown in Fig. 9 as a function of illumination intensity, F , for temperatures between 75°C and 300°C. At each temperature, the sample was initially irradiated with the largest illumination intensity for a time sufficiently long for light-induced defect

density to achieve a steady-state value. The intensity dependence of the photoconductivity, $\sigma_{ph}(F)$, is described by

$$\sigma_{ph} \sim F^\gamma, \quad (4)$$

where γ is a temperature dependent exponent. Below 150°C, $\gamma \approx 0.8-1$ and the photoconductivity, and the photo-generated electronic density, increases approximately linearly with the carrier generation rate. The exponent decreases with increasing temperature and reaches a value of $\gamma \approx 0.4-0.5$ between 200 and 300°C.

The diffusion coefficient is

$$D = v a^2 / 6 \quad (5)$$

where v is the excitation rate and a the mean free path. Normal diffusion is controlled by trapping and release from silicon-hydrogen bonds. The excited hydrogen migrates through shallower traps, so that an alternative description of the diffusion is

$$D = N_{HS} D_{HS} / N_H \quad (6)$$

where N_{HS} and D_{HS} are the density and diffusion coefficient of H in the shallow sites and N_H is the total H concentration. Possible mechanisms of light enhanced diffusion are the increase of the excitation rate, v , a change in the mean free path or alternatively an increase in the diffusion rate in the shallow states.

Two mechanisms of light enhanced diffusion suggest themselves, both related to models of metastable defects. First, the recombination of electron-hole pairs releases energy and may induce the excitation of hydrogen from an Si-H bond. Second, the presence of excess electrons and holes may change the hydrogen diffusion coefficient, perhaps by modifying its charge state. The enhancement in hydrogen diffusion under illumination has many aspects in common with light-induced defect formation in a-Si:H. The generation mechanism of light-induced defects involves recombination of photo-generated electron-hole pairs. The relative changes in the defect density in doped and in compensated a-Si:H induced by illumination is significantly smaller than in undoped samples, consistent with the lower light-enhancement of the diffusion coefficient in doped and compensated samples. The relationship between hydrogen diffusion and defect generation can be described by the following chemical reaction:

A silicon-hydrogen complex (Si-H) dissociates in the presence of photo-generated electrons (e) and holes (h). In the dissociation process, hydrogen is released and a silicon dangling-bond (Si-) is created. The released hydrogen atom diffuses through the amorphous network until it is trapped in a dangling-bond, reverting the defect creation process. Alternatively, the diffusing hydrogen can be inserted into a silicon-silicon bond (Si-Si), resulting in the formation of a second dangling bond in the right-hand-side of the reaction.

In this model of light-induced defects, the generation rate is proportional to the product np of the densities of photo-generated electrons (n) and holes (p). If hydrogen motion is involved in defect creation the diffusion mechanism should also be proportional to np . The photoconductivity data of Fig. 9 show that during the diffusion experiments, $n \approx G^{1/2}$. Assuming a similar illumination intensity dependence for the hole density, we obtain $D \sim np \sim G$, in agreement with the experimental results.

The diffusion temperatures are above the defect equilibration temperature of $\sim 200^\circ\text{C}$ in undoped a-Si:H, so that defect creation and annealing times are small compared to the diffusion times. The concentration of the different species in Eq. 1 are then expected to have their chemical equilibrium values during diffusion. From the law of mass action, the dangling bond concentration, $N_s = [(\text{Si}-)]$, is related to the carrier densities by: $N_s = K_1 np$, where K_1 is a temperature dependent factor. This expression neglects the small changes in the concentration of silicon-silicon and of silicon-hydrogen bonds during defect generation. The defect density under illumination is expected to be sufficiently high for the photo-generated carrier density to be determined by monomolecular recombination, i.e., $n \sim p \sim F/N_s$. As a consequence, $N_s \sim G^{1/2}$ and $\sigma_{ph} \sim n \sim G^{1/2}$, in agreement with the photoconductivity results for temperatures above 150°C .

According to Eq. 1, the diffusion coefficient is proportional to the density of hydrogen atoms in mobile states, i.e., $D \sim [H] \sim K_2 np/N_s \sim F$. This reproduces the linear dependence on illumination intensity displayed in Fig. 9.

B. Field dependence of the H diffusion

In order to investigate the effects of carrier density on hydrogen diffusion, SIMS studies were performed on p-i-n amorphous silicon photodiodes with a deuterated (a-Si:H:D) layer inserted in the middle of the intrinsic layer. The photodiodes were deposited on chromium-coated crystalline silicon substrates and have a top contact

consisting of a transparent ITO (indium-tin-oxide) window covered by a chromium grid. The a-Si:H layers were grown by rf glow discharge decomposition of pure silane at 200°C. The photodiodes are excellent structures for investigating the interaction between hydrogen migration and electronic carriers since the carrier concentration in the intrinsic layer can be controlled by varying either the temperature, the external bias, or the illumination intensity. In the diffusion experiments the diodes were annealed at temperatures in the range from 200°C to 275°C for times of a few hours up to several days in the dark or under illumination with water-filtered light from a xenon arc-lamp.

A representative deuterium depth profile from SIMS for an unannealed diode is illustrated by the dotted lines in Figs. 10a and 10b. The top contact layers were removed prior to the SIMS analysis. The n- and p-type doped layers were also deuterated in these samples, and the various amorphous silicon layers can be readily identified by their different deuterium contents.

The thin solid lines in Figs. 10a and 10b show the deuterium concentration in a control sample annealed under open circuit conditions (oc) for 10 days at 225°C (Fig. 10a) and for 11 h at 275°C (Fig. 10b). Under open circuit conditions, diffusion leads to a symmetrical broadening of the composition profile at the interfaces due to deuterium diffusion. The deuterium profiles are well represented by a complementary error function (erfc) characteristic of a concentration independent diffusion coefficient.

The thick lines in Figs. 10a and 10b are the corresponding profiles after annealing under the same temperature and time conditions as above, but under an applied reverse bias of 5V (corresponding to an average electric field $E = 1.3 \times 10^5$ V/cm in the intrinsic layer). The diffusion profiles at both sides of the a-Si:H:D layer differ appreciably from an erfc and consist of two parts:

- in the immediate vicinity of the edge (i.e., for deuterium concentrations above 10^{19} cm⁻³) the shape of the deuterium profiles is almost indistinguishable from that of an unannealed sample (dash-dotted line) and is determined by the SIMS depth resolution. This indicates that deuterium diffusion is strongly suppressed by the application of a reverse bias.
- for lower concentrations, a tail develops extending towards the doped layers. The tails penetrate further into the a-Si:H layer than for diffusion under short-circuit conditions, which indicates enhanced deuterium migration. Note, however, that the

FIG. 10. Deuterium diffusion profiles after annealing at (a) 225°C for 10 days and (b) 275°C. The dashed lines are the profiles for an as-grown sample. The thin and thick solid lines represent profiles for samples annealed under open circuit (oc) and under a reverse bias of -5V, respectively.

number of deuterium atoms forming the tails is a small fraction ($<10\%$) of the number of atoms diffusion under the same conditions under open circuit. In addition, the deuterium concentration decays approximately exponentially with distance, in contrast with the erfc-like profile characteristic of diffusive motion.

The combined effects of illumination and bias on deuterium diffusion is illustrated in Fig. 11. The thin solid line shows the diffusion profile for a diode irradiated under open-circuit conditions with $19\text{W}/\text{cm}^2$ during the thermal treatment. The dashed line reproduces the corresponding profile for annealing under similar conditions in the dark. Under illumination the profiles are considerably broadened at the interfaces, which indicates enhanced diffusion. The thick line in

FIG. 11. Deuterium profiles after annealing at 250C for 20h under open circuit (oc) conditions (dashed line), under oc and illumination (thin solid line), and under illumination and a reverse bias of 5V (thick line).

Fig. 11 shows the combined effects of illumination and of an average (reverse bias) field of 9.2×10^4 V/cm in the intrinsic layer during annealing. The diffusion profiles are very asymmetric with respect to the center of the aSi:H:D layer and no change is observed on the right-hand side of the deuterated layer. On the left-hand side, on the other hand, light-enhancement of hydrogen diffusion is completely suppressed under an electric field. The asymmetry in the deuterium profiles at the left and right hand sides of the deuterated layer in Fig. 11 is attributed to an inhomogeneous electric field distribution in the intrinsic layer of the photo-diodes.

Hydrogen migration in a-Si:H is controlled by hydrogen trapping and release from silicon-hydrogen bonds. The effective diffusion coefficient D_{eff} includes two components: (i) deuterium diffusion in a transport path consisting probably of mobile interstitials and/or bond center sites and (ii) the capture and release of hydrogen at trapping sites consisting of Si-H bonds. We attribute the changes in the diffusion coefficient to variations in the carrier density in the intrinsic layer of the

photo-diodes induced by either bias or illumination. Hydrogen emission from a bond can occur through purely thermal excitation to the mobile state. However, the release rate of hydrogen from Si-H bonds into the transport path is increased in the presence of photogenerated carriers through a (temperature dependent) electronic mechanism, while the hydrogen mobility in the transport path is not substantially affected. As a consequence, if the carrier density is increased by illumination, the deuterium release rate and, hence, the effective diffusion coefficient are enhanced.

The data in Figs. 10 and 11 reveal a further aspect of the diffusion process, namely that the electronic mechanism also controls hydrogen migration in the absence of external bias and illumination. As a result, hydrogen motion is suppressed when the carrier concentration in the intrinsic layer is reduced below the thermal equilibrium value by the application of a reverse bias. The interaction between carriers and the silicon-hydrogen bonds which control diffusion is probably mediated by direct recombination of electron-hole pairs, which may provide the energy necessary for hydrogen excitation from a silicon-hydrogen bond. Since hydrogen emission results in the formation of silicon dangling bonds, metastable defect generation and annealing are expected to be mediated by hydrogen migration. For example, we attribute the suppression of light-induced defect generation observed in reverse biased solar cells to the suppression of hydrogen motion when carriers are extracted from the junction.

The dependence of the release rate of hydrogen from Si-H bonds on charge carriers cannot account for the tails observed in the deuterium profiles in Fig. 9a and 9b. These tails are formed by deuterium atoms emitted from S-D bonds in the a-Si:H:D layer that migrate fast through the transport states before being captured into deep states in the a-Si:H layers. One possible explanation is that deuterium migrates as a charged species and drifts under the field. This mechanism requires the rather improbable existence of both positively and negatively charged atoms in approximately equal densities, since the tails are observed on both sides of the deuterated layer. Moreover, the density of charged species must be considerably higher than that of neutral ones. A more likely mechanism is that not only the emission from deep traps but also the capture probability is reduced under an applied field. This can happen if the effective barrier for capture and/or the density of capture sites depend on carrier density. In this case, the lifetime in the transport path is enhanced and the atoms can migrate further before being captured.

C. Concentration dependence of the H diffusion

We have experimental evidence for an enhancement in hydrogen diffusivity in a-Si:H with hydrogen concentration. The concentration dependence is attributed to the saturation of the density of hydrogen traps consisting of Si-H bonds with increasing hydrogen concentration.

The profiles in Fig. 12 compare exposure an a-Si:H film to a deuterium plasma with normal diffusion from a deuterated layer. The deuterium concentration near

FIG. 12.(a) Deuterium concentration profile after annealing for 9 h at 275C. The remaining curves are concentration profiles for (b) deuterium, (c) hydrogen, (d) hydrogen plus deuterium, and (e) ^{28}Si in an a-Si:H film exposed to a deuterium plasma for the same temperature and time.

the surface with the plasma reaches 10^{22}cm^{-3} and is significantly larger than for diffusion from a deuterated layer. In addition, a careful analysis of the shape of the deuterium profile in Fig. 1b indicates that it is well represented by an erfc only for concentrations above 10^{21}cm^{-3} (see dashed line), but then decays faster than an erfc for lower deuterium concentrations.

The most important difference between diffusion from a deuterated layer (Fig 12a) and from a deuterium plasma (Fig. 12b) is that the diffusion length is significantly larger in the second case, which indicates faster deuterium migration. This is specially true for diffusion temperatures below 250°C, where negligible diffusion from a layer is observed in a time scale of a few hours. For diffusion from a layer the diffusion coefficient has an activation energy of 1.2 to 1.3 eV and is at least an order of magnitude smaller than diffusion from the plasma for temperatures below 300°C. The activation energy for diffusion from the plasma (0.5 eV) but the diffusion pre-factor is significantly smaller than for diffusion from a layer.

Curve (c) in Fig. 12 is the hydrogen concentration profile in the sample exposed to the plasma. The hydrogen concentration decreases near the surface due to hydrogen out-diffusion during deuterium incorporation. This result indicates that during exposure to the plasma (i) the surface barrier for out-diffusion is reduced, and (ii) the diffusivity of the hydrogen originally in the sample is enhanced. The total concentration of hydrogen plus deuterium, calculated by adding curves 12b and 12c, is indicated in Fig. 12d. Except in the first 20 nm near the surface, where the profiles are distorted by the finite SIMS resolution, the total concentration of deuterium plus hydrogen in the deuterium-rich layer is up to a factor of two larger than the original hydrogen concentration. The loss of hydrogen due to out-diffusion is, therefore, over-compensated by the diffusion of deuterium from the plasma, leading to a net increase in the total concentration of the two species.

A schematic energy distribution of silicon-hydrogen configurations controlling hydrogen migration is shown in Fig. 13. Most of the hydrogen in aSi:H is located in the deep traps of energy E_t . The basic migration step consists in the excitation of hydrogen from these traps into shallow states with low binding energy E_s . The shallow states are probably interstitials and/or bond center sites where hydrogen can diffuse easily by excitation over a barrier of height $E_m - E_s$, where E_m represents the minimal energy for free hydrogen motion in the network. Any disorder-induced broadening of E_m , which is taken to be the energy reference, has been neglected in Fig. 13. Migration stops when hydrogen is re-capture into a deep state.

The population of the different levels in Fig. 13 is described by a hydrogen chemical potential, μ_H , which is slightly above the deep trap level, E_t . During diffusion from a deuterated layer the occupation of deep traps is kept constant since the hydrogen concentration is uniform through-out the sample. Diffusion is limited

FIG. 13. Schematic representation of the density of states (DOS) for hydrogen in a-Si:H

by hydrogen emission from the deep traps and the diffusion activation energy corresponds to the trap depth $E_t \sim \mu_H = 1.2 - 1.5\text{eV}$.

Diffusion from the gas phase differs from the previous case because the total concentration of hydrogen plus deuterium increases during diffusion, as shown in Fig. 12. Diffusion can be substantially enhanced if the deep traps are saturated with extra deuterium atoms injected from the plasma. Under these circumstances, deuterium lifetime in the shallow traps is substantially enhanced. Transport in this case is limited by hydrogen diffusion through weakly-bonded interstitials sites. The activation energy of 0.5 eV measured for diffusion from the plasma corresponds to the barrier height $E_m - E_s$ for migration in the shallow states. This activation energy is close to that for hydrogen diffusion in crystalline silicon, indicating that the average barrier height for diffusion is essentially the same in the two materials.

The enhancement in diffusivity of deuterium atoms injected from the plasma takes place when the total concentration of hydrogen plus deuterium in the deuterium-rich layer surpasses the original hydrogen concentration in the film by a factor of 1.5 to 2. The maximum concentration of deep traps is, therefore, of the order of 10^{22} cm^{-3} . This concentration is much larger than that of dangling-bonds, and depends on the deuterium concentration in the plasma. The deep traps near the surface are probably formed dynamically during diffusion by the insertion of a pair of hydrogen atoms in silicon-silicon bonds. No extra dangling bonds are formed in this process.

2. MODELS OF HYDROGEN BONDING STRUCTURE AND DIFFUSION.

There is strong circumstantial evidence for the role of hydrogen in the metastability. The following sections consider the hydrogen bonding distribution, chemical reactions and energetics, and apply these results to models for metastability and growth of films.

A. Hydrogen in weak bonds

Strained or weak Si-Si bonds feature in models of defect creation and metastability in a-Si:H. Defect creation by Si-Si bond breaking is expected to occur at the weakest bonds because the defect formation energy is lowest. It has further been proposed that the broken bond is stabilized through attachment of hydrogen by a reaction of the type,

where $\bullet\text{Si}$ and $(\text{Si-Si})_s$ represent a dangling bond and a strained bond. This model is based on the supposition that hydrogen binds more strongly to a strained Si-Si bond than to a normal bond, and that the H site is increasingly asymmetrical as the distortion of the bond is increased. The effects of bond strain on the hydrogen bonding energy is therefore of interest to studies of both the hydrogen diffusion and defect metastability in a-Si:H.

We have performed calculations of the hydrogen bonding in strained Si-Si bonds. The shear strain was introduced into the unit cell using the following method (see Fig. 14). One particular bond in the unit cell is labelled B, and is defined by two atoms each of which have three back-bonding atoms. We imposed a transverse strain by moving these back-bonding atoms transverse to the $\hat{a}$ direction, which is the original orientation of bond B. This movement was frozen into the back-bonding

FIG. 14. Illustration of the configuration used to introduce strain. The filled circles indicate Si atoms moved to induce strain, and the unfilled circles indicate the resulting "strained" Si atoms with a strained bond B. The displacement is parametrized in Δ . $\hat{a}$ indicates the original direction of bond B. Δ^* indicates the lateral distance between the two strained Si atoms (perpendicular to $\hat{a}$), and L indicates the longitudinal distance (parallel to $\hat{a}$).

atoms which were then not allowed to relax. All other Si atoms in the unit cell were allowed to relax. The imposed strain was parametrized in the variable Δ , the relative displacement of the two sets of back-bonding atoms. Due to the relaxation, the atoms forming bond B may have a smaller lateral displacement, which we denote by Δ^* ; the longitudinal distance is denoted by L.

The H atom was placed in one of two positions, the symmetric position, or the asymmetric position. The H atom cannot relax in the former position (the forces are 0 by symmetry), but is allowed to relax fully from the latter. Three calculations were performed: Total energy and electronic states as a function of the stress: (i) without H, (ii) with H in the symmetric position, and (iii) with H in the asymmetric position.

The charge of the unit cell in these calculations was 0, +1 and +1, respectively. One calculation is reported also for a neutral H configuration.

The calculation is of the change in strain energy due to migration of the H atom to the strained Si-Si bond:

where N and S represent normal and strained bonds. This is a general model for the particular reaction in Eq. (1). The resulting energy change for Eqn. (2) is shown in Fig. 15. For both the symmetric (results always indicated with filled *circles*) and

FIG. 15. Energy gained in the reaction described in Eq. (9). Triangles label asymmetric configuration and the circles the symmetric configuration.

asymmetric (results always indicated with filled *triangles*) configurations, there is energy gained when the H atom is transferred from a normal bond to a strained bond. The energy is about 0.4 eV for a Δ of 1 Å. We also find that the asymmetric site is more favorable than the symmetric site. The energy difference between the two is 0.1 eV for a Δ of 1 Å, increasing to about 0.7 eV at $\Delta=2$ Å.

The H induced strain energy reduction changes the response of the atomic configurations. Fig. 16 compares the lateral distance, Δ^* , which the strained Si atoms move (vertical axis) with the lateral distance Δ imposed on the back-bonded Si atoms (horizontal axis). The actual distance moved would be linear in the imposed

FIG. 16 .Lateral distance Δ^* of the strained Si atoms as a function of imposed displacement Δ . Squares label distances from the configuration without H, circles label distances from the symmetric configuration, and triangles label distances from the asymmetric configuration.

distance if the material can easily accommodate the imposed stress, and we expect an increasing deviation from linearity Δ - Δ^* as the strain builds up. Fig. 15 shows that in the presence of an H atom, the imposed and actual distances are very close, with the asymmetric being the closest. In the absence of H (these results are always be indicated with filled *squares*) there is a significant deviation.

We also examined the actual *longitudinal* distance L moved as a function of Δ . The configurations with H start out at as bond-centered sites, for which the distance L is initially about 3.2 Å. The change in longitudinal distance is linear for the asymmetrically placed H atom. The distance decreases to release the stress imposed by including the bond-centered H. This change in position is about 0.2 Å for a Δ of

1Å. Symmetry imposes that the change is quadratic for either symmetrically placed H or no H at all. We note that the symmetrically placed H is not able to release the longitudinal strain as well as the asymmetrical configuration.

Models of hydrogen in a-Si:H have assumed that hydrogen bonding is stronger at distorted Si-Si bonds, and that the bonding site is highly asymmetrical at the most strained sites, approximating to an Si-H bond and a dangling bond rather than a bond center site. The calculations confirm both of these suppositions. The asymmetrical site is favored by up to 1 eV and the electronic states in these sites have the character of a silicon dangling bond.

The variation of hydrogen binding energies in a-Si:H can be described by a hydrogen density of states distribution. The calculations allow an estimate of this distribution, by relating the bond angle disorder in a-Si:H to the strain induced changes in the H bond. We assume a gaussian distribution of bond angle deviations, $N(\theta)$, with distribution σ , about the normal tetrahedral silicon bonding. The bond angle deviation is about 10° , as obtained from X-ray measurements of the silicon radial distribution function;

$$N(\theta) = N_0 \exp[-\theta^2/\sigma^2] \quad (10)$$

The bond angle deviation is related to the strain introduced in the calculations, approximately by Δ/R , where R is the bond length, $2.35\text{\AA}$. The energy shift, E_H , of the hydrogen bond in Fig. 3 is roughly parabolic and may be described by,

$$E_H = \alpha \Delta^2 \quad (11)$$

with $\alpha \approx 0.4 \text{ eV}\text{\AA}^{-2}$. The distribution of the hydrogen bond energy is therefore,

$$N(E_H) = N_0 \exp[-E_H/E_0] \quad (12)$$

where, $E_0 = \sigma^2 R^2 \alpha \approx 100 \text{ meV}$ (13)

Thus, we obtain an exponential hydrogen distribution with an inverse slope of 100 meV. This distribution is close to the estimates made previously for the hydrogen density of states in a-Si:H, which were based on simple models of weak bond breaking.

B. H bonding models for growth of alloys

The properties of plasma deposited a-Si:H and its alloys depend on deposition conditions such as substrate temperature, rf power, gas composition etc. Progress has been made in identifying the complex chemical reactions which occur during

growth, and the conditions for optimum films. However, a causal connection between the plasma chemistry and the electronic properties has not been made. The main parameters governing the electronic properties are the slope of the valence and conduction band tails and the defect density, which is less than 10^{16} cm^{-3} in good a-Si:H.

The model discussed in this paper relates the growth to the electronic properties, by focussing on the role of hydrogen rather than the gas radicals. The model assumes that the electronic structure of the film is formed in the subsurface region by the process of hydrogen elimination and cross-linking of the Si-Si bonds. The structure is conveniently described in terms of the hydrogen density of states distribution, (HDOS), which is shown in Fig. 17. The important features are the Si-H

FIG. 17 . Illustration of the HDOS for a-Si:H, showing the Si-H bonds and the energy of H in the distribution of Si-Si bonds. E_M is the effective migration energy of H in a-Si:H; μ_H is the hydrogen chemical potential; and E_R is the redistribution energy as defined in the text.

bonds, the distribution of weak and normal Si-Si bonds, of which the weakest are the lowest energy bonding sites for hydrogen, the energy E_M where hydrogen migrates, and the chemical potential, μ_H . In the ideal material, H terminates all

dangling bonds and the number of weak Si-Si bonds is minimized. This occurs when the distribution of bonds is as close as possible to equilibrium, with minimum disorder constrained by the amorphous network. Defects form at states near the chemical potential, so that μ_H of optimum films lies in a minimum of the HDOS. The growth conditions influence the HDOS through the tendency to align μ_H in the film and in the plasma.

A low equilibrium defect density requires that almost all the Si-H bonds are occupied by hydrogen and therefore that μ_H lies above the Si-H band in the HDOS. The equilibrium defect density is,

$$N_{DH} = \int N_H(E)[1-f(\mu_H, E, T)]dE \quad (14)$$

where f is the Fermi function. A defect density of 10^{16} cm^{-3} at a temperature of 250°C requires that μ_H is above the Si-H band by at least 0.5 eV.

When radicals attach to the surface the structure is disordered and highly hydrogenated, with a HDOS. The change in the HDOS is attributed to hydrogen reactions in the subsurface region. The rate limiting step in these reactions is assumed to be the excitation of hydrogen to a mobile state allowing diffusion and reconstruction of the network. The time for thermal excitation of hydrogen from energy E is

$$t = \omega_0^{-1} \exp[(E_M - E)/kT] \quad (15)$$

A redistribution energy, E_R , is defined by the time, t_s , available for structural change,

$$E_M - E_R(T) = kT \ln(\omega_0 t_s) \quad (16)$$

Hydrogen occupying states above E_R in the HDOS is excited in time t_s , while the more tightly bound hydrogen is not. The time t_s is that required to grow the film to the thickness of the subsurface region, and may be 10^{-10} sec. An assumption of the model is that optimum film growth requires that most of the hydrogen atoms redistribute, and therefore that E_R lies below E_H .

The growth is kinetically limited when most of the H is below E_R , and the subsurface reactions are only partially complete. The film contains vestiges of the deposition radicals, in the form of $=\text{SiH}_2$ and $-\text{SiH}_3$ structures. The kinetic limit is exceeded at $200\text{-}250^\circ\text{C}$ for a-Si:H, when $E_M - E_R \approx 1.5 \text{ eV}$.

The two conditions for growth of good quality films are therefore (1) that μ_H lies significantly above the Si-H band and (2) E_R lies below this band. The temperature dependence of μ_H and E_R and define a range of optimum growth temperatures.

Binary alloys of a-Si:H provide control over the band gap of the material. Hydrogen binds to both alloy elements with different energies. Alloys are classified depending on the strength of the hydrogen bond to the alloy element compared to Si-H. Type 1 alloys have stronger bonds, (eg a-Si:C:H, a-Si:O:H and a-Si:N:H); Type 2 alloys have weaker bonds (eg a-Si:Ge:H).

- Type 1 Alloys (a-Si:C:H)

The schematic HDOS of a-Si:C:H in Fig. 18 shows the separate Si-H and C-H bands which differ in energy by about 1 eV. The difficulty in growing these alloys is readily

FIG. 18. Illustration of the hydrogen density of states for (a) Type 1 (a-Si:C:H) alloys, and (b) Type 2 (a-Si:Ge:H) alloys, showing the different hydrogen bonding states.

apparent. The requirement that μ_H lies above the H bonds and E_R is below, is more constraining because of the large separation of the Si-H and C-H bonding energies.

The growth conditions used for a-Si:H, do not allow a rearrangement of the C-H bonds which lie below $E_R(250^\circ\text{C})$. The C-H bonds are kinetically limited and cause a disordered structure. Hence, the model explains why a-Si:C alloys have a broad valence band tail which increases with carbon concentration. Further, the model predicts the presence of $=\text{CH}_2$ and $-\text{CH}_3$ bonding structures due to the kinetic limitation, which are observed. The broader band tails lead to a larger defect density in a-Si:C:H, according to the weak bond model. The HDOS shows that the Si-H band is closest to μ_H , and therefore Si dangling bonds are expected to be the dominant defect with few carbon dangling bonds, again in agreement with experiment.

The model suggests that deposition under conditions of high temperature and high hydrogen dilution might improve the film quality. The kinetic limit is removed by deposition at high temperature. The decrease in the chemical potential with increasing temperature tends to raise the defect density. However, the energy of μ_H may be maintained by dilution of the plasma with hydrogen.

- Type 2 Alloys (a-Si:Ge:H)

The HDOS of the Type 2 alloys is shown in Fig. 18b. The weaker H bond of the alloy element implies that the structural rearrangements are determined by the Si-H bonds, and growth at 250°C is not kinetically limited. The model predicts that the band tail distribution is similar to that for a-Si:H (apart from a contribution from alloy bonding disorder), and indeed, a-Si:Ge:H alloys are grown with band tails which are little different from a-Si:H.¹⁰ Instead, the problem with growth of these alloys is that the Ge-H band overlaps the weak bond distribution. The chemical potential lies in a large density of states, resulting in a high defect density. The defects are expected to be Ge dangling bonds because the Ge-H band is at the higher energy, and this agrees with experimental observations.

Improving the electronic properties of Type 2 alloys is difficult because of the overlap between the weak bonds and the Ge-H bonds in the HDOS. The model predicts that growth of low defect density material requires careful control of the hydrogen chemical potential, and that the range of suitable growth conditions is more constrained than for a-Si:H. Hydrogen dilution of the plasma and lower temperature deposition may help to raise μ_H . Optimum conditions are expected to be close to those needed to grow microcrystalline material.

C. The H density of states and models of H Diffusion

Hydrogen traps are believed to be either isolated dangling Si bonds or larger clusters of H ranging from pairs to large extended H platelet structures and/or hydrogenated voids. In order to elucidate the nature of the H traps, the effect of H concentration and previous thermal history is investigated. The experiment consists of introducing deuterium (D) from a remote H plasma into various films and measuring the H and D concentration profiles using secondary ion mass spectroscopy (SIMS).

In Fig. 19, the D and H profiles for a rehydrogenated sample with varying

Fig. 19 D and H concentration profiles for rehydrogenated H depleted samples at 340 °C 1hr. The dashed line indicates a complementary error function profile. The thin line represents a sample which was rehydrogenated by a high concentration of H while the thick line is for an H depleted sample.

amounts of H are shown. For D concentrations exceeding $4 \times 10^{20} \text{ cm}^{-3}$, the diffusion profiles are independent of H concentration. Below this level, the profiles depend on H concentration. Both curves depart from an error function profile (erfc) indicated by the dashed line and become exponential, a form characteristic of diffusion in the presence of deep traps. [8] The trap density in the bulk of the a-Si:H film can be estimated from the concentration at which the profile departs from the erfc profile. The trap density in the high H concentration material is about 2.8×10^{20}

cm^{-3} and only $6 \times 10^{19} \text{cm}^{-3}$ for the low H films. In both cases, the number of traps appears to be comparable to the H concentration in the film.

The profiles for an annealed series of samples are presented in Fig. 20. The

Fig. 20 D profiles for samples annealed for indicated number of hours at 350 °C. The samples in set A were exposed at a higher D concentration than set B. The least square complementary error function fits to the high concentration regions are indicated along with the H concentration for the two sets of samples

interesting features of these curves are the effect of annealing on the low concentration regions and the absence of effects at high concentrations. The low concentration exponential tail indicates the presence of deeper traps in the concentration of $1 \times 10^{21} \text{cm}^{-3}$ for the high D series and $4 \times 10^{20} \text{cm}^{-3}$ for the low D series. The H concentration varies in a similar fashion. Combining this data with the data on the rehydrogenation samples we find that the H deep trap density is a fraction in the range of 20% to 80% of the total equilibrated H concentration.

Since the deep traps are a roughly constant fraction of the existing equilibrated bonded H, the chemical potential, μ_H separating the occupied from the unoccupied states (traps), must stay in a roughly fixed relation to the equilibrated bonded H configurations as the H content is increased. The effect of increasing the equilibrated bonded H on the H DOS is indicated in Fig. 21. the data show that annealing results in deeper traps since the emission rate decreases. This increase in trap depth, presumably of bonded H, may account for the dispersive H diffusion observed as the energy to the transport state increases over time. When H (or D) is introduced from the plasma in sufficient concentrations, μ_H moves upwards

Fig. 21 Effect of H concentration and annealing on H DOS. Increasing the H concentration results both in more bonded H and more traps (unoccupied states) without changing the properties greatly. Annealing primarily causes the traps and perhaps the bonding to decrease in energy while maintaining roughly the same number of traps. A large supply of exogenous H from a plasma causes a temporary increase in the chemical potential shown.

temporarily giving rise to the enhanced H diffusion at high concentrations. At longer times the chemical potential tends to return to its previous level.

While the previous discussion provides a description of results in term of H DOS and chemical potentials, the origin of the effects are unspecified. We propose that nucleation and growth of large H clusters can account for these effects, realizing that much work needs to be done to further investigate this possibility. We propose that H resides largely in clusters. The energy of the cluster depends on the number of H pairs ($n=1$) within the cluster. The energy per H atom decreases as n goes from 1 to ∞ . All clusters whose energy per H is greater than μ_H are unstable and therefore dissociate. Even among the clusters with energies below μ_H the larger clusters are energetically favored over the small ones. As a result, small clusters tend to disappear and be replaced by larger clusters given enough time. In effect, μ_H will tend to reside in a minimum in the H DOS regardless of the H concentration provided that the isolated configurations are removed. The H cluster model therefore provides a microscopic mechanism for the proposal that the H chemical potential lies within a DOS minimum.

Long time annealing at 350 °C causes the more stable large clusters to grow. The increase in cluster size decreases the H average energy and lowers μ_H . Exogenous H which has time to equilibrate (e. g. the H introduced at 430 C for 2.5 hrs) attaches to the larger clusters below μ_H . A certain fraction of clusters with H binding energies at

or above μ_H always remains since this is a driving force for larger cluster formation. These sites as well as the sites near the cluster edges serve as deep traps for H and therefore their concentration scales with increased H concentration. Hence, this model can account for the increased trap depth upon annealing as well as the increase with H concentration.

The transient changes due to H or D added from the plasma can also be understood with this model. If H is added in relatively large concentrations at comparatively short times, the H only has time to form small clusters causing μ_H to increase significantly towards the transport level. Consequently the diffusion is rapid. The chemical potential position and H bonding are primarily determined by the interstitial H concentrations and the kinetics of small cluster formation, factors determined by the H flux and overall properties of the silicon network. Diffusion in this regime is therefore rather independent of the details of the silicon network.

3. ELECTRONIC PROPERTIES.

A. Transport at high electric fields

The high field transport properties were measured by TOF on a-Si:H p-i-n junctions of thickness 2 and 10 μm . A pulsed reverse bias was applied and a transient current was created by a short (3 ns) laser flash.

Charge collection measurements displayed in Fig. 22 show that in order to achieve full collection within the time window $t < 10^{-5}$ s, the field has to be larger than $F > 3.5 \times 10^5$ V/cm without any indications of carrier multiplication up to $F \leq 5 \times 10^5$ V/cm (the highest accessible field). A higher excitation level (9×10^{-9} C) creates space charge distortions at low fields, which gives rise to the difference in field dependence of the two data sets. The $\mu\tau$ -product of 3×10^{-9} cm^2/Vs is only a factor of 200 smaller than the room temperature value; it, however, much larger than the value deduced from DC-photoconductivity experiments at considerably smaller fields (10^{-13} - 10^{-12} cm^2/V). The sudden on set and steep rise of Q for $F > 10^5$ V/cm are significant features of low T and high field experiments. The increase of μ_D which follows a $\mu_D \sim F^\gamma$ law where $\gamma \approx 11$, together with the high $\mu\tau$ -product, points towards a drastic change of transport mechanism in the presence of high fields.

Electron drift mobilities are shown in Fig. 23. μ_D monotonically decreases at lower temperatures and fields with no relative or absolute minimum. The activated

FIG. 22. Charge collection and drift mobility data for the 10 μm p-i-n junction measured at 40 K (two laser excitations: 9×10^{-9} C and 9×10^{-11} C).

behavior of μ_D at low temperatures (E_{act} is in the range of 10 to 50 meV, decreasing to $\sim kT$ at 40 K) indicates that there is a shrinking separation between transport path and center of charge. The surprisingly high mobilities of electrons in the presence of high fields, the power law dependence and the slowed down current decay indicate a transport mechanism which is effective even at such low temperatures.

We also find a drastic impact of high electric fields on the conductivity (σ) of phosphorus- and boron-doped samples at low temperature. Doping introduces enough carriers (referred to as band-tail carriers nBT) to shift the onset of space charge limited currents beyond the highest voltage used (≤ 100 V) and the Fermi level is in the tail region. The measurements have been performed on n+-n-n+ and p+-p-p+ sandwich configurations, where the highly doped 30 nm thick layers (n+, p+) guarantee ohmic behavior. The thickness of the n or p layer has been varied between 1-3 μm and the doping level between 10^{-2} , 10^{-3} , and 10^{-4} PH_3/SiH_4 (referred to as P2, P3, P4) and 10^{-2} and 10^{-3} $\text{B}_2\text{H}_6/\text{SiH}_4$ (referred to as B2, B3),

FIG. 23. Drift mobility of electrons as function of temperature (T) and electric field (F) in a-Si:H.

respectively. We also performed pulsed field experiments to check the current/voltage characteristic, and this confirm the DC data.

Fig. 24 shows the field dependent conductivity measured at $T = 40$ K for different doping levels and dopants (P,B). The conductivity changes by 8 orders of magnitude in the presence of high electric fields, and can be described by a power law

$$\sigma \sim F^\gamma \quad (17)$$

The higher the doping, the lower the critical field necessary to achieve high conduction. With increasing doping, γ decreases from ≈ 15 (P4) to ≈ 13 (P3) and ≈ 11 (P2), and from ≈ 16 (B3) to ≈ 15 (B2), respectively.

The Fermi level which is in the band tail region at low T and high doping levels determines the field strength necessary to enhance the conductivity. This is shown by performing quenching-in experiments (annealing the sample at 230° C for 20 min,

FIG. 24. Field enhanced dark conductivity of phosphorus and boron doped a-Si:H at 40 K.

followed by a fast water cooling to room temperature). Due to the activation of additional dopants at high temperatures and the fast cooling which freezes in a non-equilibrium electronic structure, the number of band tail carriers can be reversibly increased, shifting the Fermi-energy closer towards the band. After quenching, the field necessary for enhancing the conductivity is considerably smaller as is γ (≈ 10) (see Fig. 24, dotted line).

To create the same enhanced conductivity in boron-doped material, the field has to be at least twice as large as in the case of phosphorus-doped a-Si:H. We explain this by the much deeper Fermi-energy in B-doped than in P-doped a-Si:H.

The temperature and field dependence of σ is shown in Fig. 25 for phosphorus-doped a-Si:H. The field enhanced conductivity has an additional thermal component at the higher temperatures, which in all cases increases the conductivity. The onset

FIG. 25. Temperature- and field-dependent dark conductivity and mobility of phosphorus doped a-Si:H. Drawn in (dashed lines) TOF mobilities.

of thermal activation of $\sigma(F, T)$ depends on F . The conductivity rapidly decreases with decreasing temperature at low fields.

The hopping transport measured by DC experiments takes place deeper in the tail than during TOF experiments. This becomes obvious by comparison of mobilities deduced from TOF and DC experiment ($\mu = \sigma / n_{BT} q$ where $n_{BT} = 10^{17} \text{ cm}^{-3}$ for P3 and $n_{BT} = 2 \times 10^{17} \text{ cm}^{-3}$ for B2, $q \equiv$ elementary charge). The TOF mobilities are several orders of magnitude larger than the mobilities calculated from the DC experiment at lower fields. Extrapolation of lines, however, show that the two sets of data fit each other surprisingly well. It is interesting to note that the γ value of the field enhanced conductivity (phosphorus-doped) approach the value deduced from TOF for $\mu(F)$.

The non-linearity discovered in a-Si:H can be reproduced nicely in doped a-Si:H. The good agreement of data related to doped and undoped a-Si:H indicates that the

change in conductivity in doped samples is not a doping effect but an inherent property of disordered materials with a high density of band tail states. Strong fields continuously increase the mobility in the tail region of a-Si:H which causes enhanced conductivity if carriers are populating the tail.

Every transition in the field direction changes the energy of the carrier by the amount $E = q \times F$ (where $x \equiv$ hopping distance). The number of accessible sites in the density of localized states is increasing considerably for a carrier and so also increases the mobility. In order to demonstrate the influence of the field on the hopping mobility for a given tail state distribution we have calculated $\mu(E,F)$ based on a numeric computer simulation. $\mu(E,F)$ decreases towards the deep tail region but is strongly enhanced by the electric field.

Field enhanced conductivity shows a Fermi-level dependence which can be explained with a modified Shapiro/Adler transport model where $\sigma(E,F) = q \mu(E,F) f(E,F) g(E)$ ($g(E) \equiv$ density-of-state distribution) with a strong field dependent mobility $\mu(E,F)$ and, up to now, without a very well defined occupation function $f(E,F)$. It is obvious that the occupation function $f(E,F)$ (which at low fields is the Fermi distribution) determines the effective conductivity σ directly, since the number of carriers within the tail region of high mobility is dependent on $f(E,F)$. A shift of E_F deeper into the mobility gap therefore significantly reduces the conductivity, especially at low temperatures where most of the carriers are close to E_F . This gives rise to the doping dependence. The significant difference between phosphorus and boron doped a-Si:H is caused mainly by the same reason. The Fermi niveau is considerably deeper in the mobility gap due to the broader valence band tail although the number of band tail carriers is comparable.

There are arguments for substituting F by a Boltzmann distribution with an effective temperature T^* , which is given by $T^* = T + \alpha q F / (2 k)$ ($\alpha \equiv$ localization length, $k \equiv$ Boltzmann constant, $T \equiv$ applied temperature). Based on this equation, the conductivity measured at different temperatures and fields can be normalized on T^* ($\sigma(T,F) = \sigma(T^*)$). We tested this assumption by plotting $\sigma(T^*)$ versus $1000/T^*$ calculated for $\alpha \approx (8-10) \text{ \AA}$. The agreement between the different sets of data is rudimentary, not only in this case but also for all the other data. The introduction of an effective temperature as a substitute for the electric field seems to be of limited validity.

B. Kinetics of dopant metastability

Dopant equilibrium is maintained by a balance between activation and passivation processes. The relaxation kinetics for small departures from equilibrium reflect both processes, while for large departures one or other dominates. Similarly, any non-linear dependence of the relaxation rate on dopant concentration is removed when the deviation from equilibrium is sufficiently small. This work explores how the equilibration kinetics depend on the departures from equilibrium, to understand the separate roles of passivation and activation on the kinetics.

DC-dark conductivity is given by $\sigma = n_c \mu_c q$ where $n_c \equiv$ carrier density above the mobility edge and $\mu_c \equiv$ extended state mobility. The conductivity is a sensitive tool to measure small metastable electronic variations in a-Si:H.

Experiments are performed on 10^{-4} PH₃/SiH₄ and 10^{-3} B₂H₆/SiH₄ doped samples of thickness 3 μ m, prepared by a conventional RF glow discharge, in coplanar contact configuration. In order to create an abrupt temperature variations, the samples were annealed in an oil bath of lower or higher temperature (T_A), for a given time to allowed the structure to equilibrate, and then rapidly transferred into a different oil bath with temperature T_M where the conductivity was monitored as function of time. This procedure enables a change of temperature within times shorter than 2 s. Typical changes of the conductivity during annealing were in the range 5 to 30%

The relaxation of P-doped a-Si:H after freezing in of an excess number of electrons shows the well known stretched exponential time dependence with β increasing from 0.65 to 0.77 with increasing T_M . The activation of dopants, in which the sample is annealed for an extended time at a lower temperature than T_M and then rapidly heated to T_M , however, is different. The creation of active phosphorus towards the new equilibrium follows a stretched exponential time dependence with a temperature independent value for the dispersion parameter $\beta \approx 0.85$.

The temperature dependence of the time constants of passivation and activation are plotted in Fig. 26, and show thermally activated behavior with $E_{act} \approx 1.1$ eV. It is interesting to note that τ related to the activation is slightly larger than τ measured from annealing out experiments. Fig. 26a shows this feature in detail where τ is plotted as function of the annealing temperature T_A . Obviously τ is decreasing with increasing annealing temperature by a factor 1.3 to 2. The effect becomes smaller at higher T_E .

Fig. 27 shows relaxation and activation kinetics of B-doped a-Si:H. The kinetics

FIG. 26. (a) Time constants to achieve thermodynamic equilibrium ($\tau_{act} \equiv$ dopant activation, $\tau_{rel} \equiv$ dopant passivation). (b) Relaxation time of phosphorus measured at T_M as function of the annealing temperature T_A .

for both are well described by stretched exponential time dependences. The dispersion parameter β is slightly temperature dependent and in the range ≈ 0.6 which fits reasonably well the overall temperature dependence of $\beta(T)$ deduced from the relaxation experiments on P-doped a-Si:H. Assuming the law $\beta = T/T_0$ results in $T_0 \approx 575$ K. β is not dependent on the degree of perturbation. Even very small deviation from equilibrium are annealed out with stretched exponential time dependence. The activation energy is about 1.1 eV, similar to P-doped a-Si:H, although the boron metastable changes are about three orders of magnitude faster than the phosphorus. τ_{act} is smaller than τ_{rel} , a fact which is displayed in Fig. 26a in more detail.

The results show interesting differences of relaxation kinetics between P and B doped a-Si:H and a dependence of the time constant on the deviation from equilibrium. Metastability of a-Si:H is believed to be related to the migration of hydrogen. According to this model, H migration occurs by thermal excitation of deep

FIG. 27. Normalized currents representing boron activation (annealed at $T_A = 336$ K) and passivation (annealed at $T_A = 388$ K) measurements.

trapped H to shallow interstitial sites where the propagation is more likely. In thermodynamic equilibrium the distribution of H is described by a Fermi-function which is governed by the hydrogen chemical potential μ_H . It is important to note that no experimental information on the detailed shape of the DOS is available as well as that the existence of a sharp transport edge is very unlikely. The later statement is supported by the stretched exponential time dependence of even smallest deviations from the equilibrium. The relaxation towards the equilibrium shows dispersive properties which indicates the involvement of several sites, spread in energy. An exponential time dependence is typical for a two level system which approximately can be detected for P activation. But even here the β value of 0.85 points towards a multi-energy step relaxation. With the assumption that the activation energy of the τ represents the energy gap between levels involved in transport and μ_H ($E_{act} \approx kT \ln(\tau(T)/\tau_0)$) we can estimate the statistical shift of μ_H by introducing the variation of relaxation times. This leads to $\Delta\mu_H \approx 20$ meV. A shift

higher (boron) or lower (phosphorus) in energy is dependent on the specific DOS adjacent to μ_H which seems to be different for B and P doped a-Si:H.

The significant difference in dopant activation kinetics between P- and B -doped a-Si:H is surprising. This can be either caused by a dopant specific weak bond DOS or (and) by the differences in local structure embedding the dopants. In the case of B the H atom inserts between B and a neighboring Si atom, bonding to Si and passivating B. In the case of P, the H is located in an antibonding site forming a bond with the Si atom, breaking the P-Si bond and removing the P donor level. In both cases we determine passivation energies of ≈ 1.1 eV which are in reasonable agreement with theoretical predictions for P-passivation are 0.95 to 1.05 eV [10] and 0.8 to 0.9 eV for B passivation.

C. Transient forward bias characteristics of p-i-n cells

Several studies of the forward bias transients in a-Si:H p-i-n diodes have found a delay in the onset of the steady state current. The delay can range from 10^{-6} up to about 1 second, depending on the sample, applied voltage, and the time between voltage pulses. Our experiments were performed on p-i-n devices. In order to explore the effect of material properties, dangling bond defects were created either with prolonged illumination or by passing a high forward current. The computer model used to interpret the data is based on a two-dimensional solution of both electron and hole continuity equations and Poisson's equation. The continuous distribution of localized states in the gap is modelled by 34 discrete levels spaced by 50 meV, and Shockley-Read-Hall statistics are assumed to describe trapping and recombination.

Figure 28 shows experimental results for the bias dependence of the current in p-i-n diodes. The current increases by 1-2 orders of magnitude after a delay time which depends on the bias. The bias dependence is summarized in Fig. 28b, which shows variations in the delay time from 10^{-6} to nearly 1 sec. depending on the level of degradation and the bias. The results of the numerical modelling for a partially degraded sample are shown in Fig. 28b. The model reproduces the experimental data quite well, giving the abrupt increase in current and the dependence on bias. Previous work has shown that the same model parameters correctly predict the voltage dependence of the final steady state current.

Figure 28b indicates that the delay time increases with defect density, and further data is shown in Fig. 29. The experimental results are obtained using defect creation

FIG. 28. (a) Voltage dependence of the forward bias transient for an undegraded p-i-n diode. (b) Experimental and computed results for the delay time for different voltages and degradation states.

by passing a forward current for the times indicated. Similar results are observed using prolonged illumination to create dangling bond defects. The delay time increases by a factor of 100 as the defect density increases from about $3 \times 10^{15} \text{ cm}^{-3}$ up to 10^{17} cm^{-3} (as measured by the reverse bias current). The current change is even more striking in the degraded samples than the annealed ones, increasing by about 1000 times. The numerical model also finds that the delay time increases and the current rise is larger in degraded samples compared to annealed material. The degradation is introduced by uniformly increasing the density of states near mid-gap in the model by the factors shown in the figure.

In the simulations shown in Fig. 29, it is assumed that the defect density is uniform throughout the bulk of the i-layer. The modelling shows that the transient current depends quite sensitively on where the defects are actually located. Fig. 30 compares results for degradation within $2000 \text{ \AA}$ of the contacts or in the middle of the i-layer. It is seen that degradation near the p-layer has very little effect on the

FIG. 29. Experimental (a) and calculated (b) dependence of the forward bias transients on the dangling bond defect density in the i-layer. The defects are created by a forward bias for the times indicated.

forward current, while degradation near the n-layer or in the middle of the i-layer has a much larger effect. These results are confirmed by experimental measurements which find that the delay time increases most rapidly for defects generated by strongly absorbed light incident on the n-type contact. We conclude that defects on the n-layer side of the sample are the most important traps for the effect.

Since the calculations successfully reproduce the effect, we can analyse the simulations to understand in detail the origin of the delay. The results show that the effect is caused by a delay in the onset of double injection. When the sample is at zero bias before the voltage pulse, there is an internal field, determined by the built-in potential of the doped contact layers and the density of states distribution. The field, $F_0(x)$, tends to be largest near the p-layer and decreases towards the n-layer, reflecting the depletion layer. Since the built-in potential is 0.5-1 V, the maximum internal field in undegraded samples is about 10^4 V/cm. Degraded samples have a

FIG. 30. Calculations of the effect on the forward bias transients on degradation in three different regions of the sample. Regions 1 to 3 are respectively, 2000Å next to the n-layer, the middle 6000Å of the i-layer and 2000Å next to the p-layer.

narrow depletion layer, resulting in a much larger field near the p-type contact and a field-free region in the interior of the sample. Immediately after the voltage is applied, the forward bias field adds with the opposite polarity to the internal field. Thus the field at the p-type contact is low, and is given by,

$$F(x) = F_A - F_0(x) \quad (1)$$

where x is the position in the sample and F_A is the applied field.

The delayed current arises because hole injection is initially prevented by the space charge barrier resulting from the zero bias depletion layer. The potential barrier is lowered by charge introduced by current flow. However, single carrier injection currents are low because of the limitations on the space charge which cannot exceed about CV , where C is the sample capacitance. The double injection current is potentially much larger, because the individual electron and hole charges can be larger than CV , but offset each other so that the net charge is within the CV

limit. Thus, when the voltage is applied there is a space charge limited current flow of electrons. The hole current occurs only when the space charge barrier is removed, and this requires the transport of a sufficient concentration of electrons from the opposite contact. As soon as the barrier is lowered, the hole injection neutralizes the electron space charge and both currents increase rapidly. The reduction in barrier height at the longer time allows the double injection current. Note that when the voltage is applied, there are barriers for both electrons and holes. Electron injection occurs first, probably due to a combination of the larger zero-bias internal field near the p-type contact, and the broader valence band tail which is the origin of the low hole drift mobility. Both effects increase the activation energy required by the holes to overcome the potential barrier.

Understanding the mechanism allows us to explain the dependence of the delay time on the various experimental parameters, as follows:

A. Degradation. The increase in delay time and the larger current rise in degraded samples occurs partly because the narrow depletion layer causes a larger barrier for hole injection. In addition, the initial space charge limited electron current is reduced by the high defect density. The low current and high defect density means that it takes longer to neutralize the space charge and enable hole injection.

B. Pulse rate. After the voltage pulse is turned off, the space charge is removed by thermal excitation of electrons and holes from mid-gap states to the band edges. Carrier release occurs over a wide distribution of times extending up to at least 100 sec at room temperature. A rapid pulse repetition rate prevents full recovery of the space charge distribution and reduces the delay time.

C. Illumination. Illumination excites electron-hole pairs and provides an additional source of charge to overcome the hole barrier and therefore reduces the delay time, as observed.

D Location of defects. Finally, the sensitivity to defects near the n-type contact follows because the electron injection is needed to reduce the space charge barrier for the holes. Defect states near the contact reduce the electron current and consequently extend the delay time.

2. INTRINSIC STRESS IN RHP FILMS.

Motivated by the need to better understand the problem of adhesion of a-Si:H films and a desire to further explore the unique properties of a-Si:H films deposited

in a remote hydrogen plasma (RHP) reactor, we have undertaken a systematic study of intrinsic stress in these films. The a-Si:H films were deposited either in a remote hydrogen plasma reactor or in an rf glow discharge system. For each case, deposition conditions known to produce electronic grade a-Si:H films were chosen. Curvature measurements were performed with quartz substrates, and infrared absorption (IR) spectra were recorded with silicon substrates.

The total stress in each a-Si:H film was calculated from the expression

$$\sigma_t = E_s t_s^2 / [6(1 - \nu_s) t_f R], \quad (18)$$

where σ_t = total film stress (by convention, a compressive film stress is negative), E_s = Young's modulus of the substrate, t_s = substrate thickness, ν_s = Poisson's ratio of the substrate, t_f = film thickness, and R = net change in substrate radius of curvature induced by the a-Si:H film. Equation (1) is true only under the following conditions^{3,4,5}: the substrate is an elastically isotropic thin plate, the film thickness is uniform, $t_f \ll t_s$, the film stress is isotropic and planar, the maximum deflection induced by the film is less than $t_s/2$.

The optical lever technique was used to measure the quartz substrate curvature before and after a-Si:H film deposition. A schematic of the experimental apparatus is shown in Fig. 31. The laser, mirror, and photodetector assembly are mounted to a translation stage which is moved by a computer controlled stepper motor. The laser beam deflects downward to the substrate by way of the mirror, then reflects off the substrate back up to the photodetector assembly, which produces electrical current signals proportional to the beam spot intensity and position. These signals are processed and collected by the data acquisition system and then sent to the computer. By translating the beam spot across a designated length of the substrate, data for beam deflection as a function of beam spot translational position is obtained. From these data, the substrate curvature is calculated.

Figure 32 shows intrinsic stress data for the RHP and GD deposited a-Si:H films as a function of deposition temperature. For the RHP material, the H_2 flow was held constant at 200 sccm while the SiH_4 flow was varied to give the ratios of 5:1 and 10:1 for $[H_2]:[SiH_4]$. The GD material was deposited in a 100% SiH_4 plasma.

For each H_2 to SiH_4 ratio, the compressive intrinsic stress in the RHP a-Si:H film increases with increasing deposition temperature, though at higher temperatures,

FIGURE 31. Schematic diagram of the apparatus for measuring substrate curvature. Optical lever arm length is 1.777m.

FIGURE 32. Intrinsic stress of a-Si:H films deposited by the remote hydrogen plasma (RHP) and rf glow discharge (GD) techniques as a function of deposition temperature. Data for two ratios of hydrogen to silane are shown for the RHP material. The hydrogen flow was 200 sccm for the RHP material. The GD material was produced in a pure silane plasma with a flow of 100 sccm.

the rate of increase slows. In contrast, the GD a-Si:H films show a maximum compressive intrinsic stress near 250°C.

In Fig. 33, the effect of PH₃ concentration on intrinsic stress in the RHP a-Si:H films is presented. For the set of films used in this figure, the deposition temperature was 400°C, the H₂ to SiH₄ ratio was 5:1 (or 0.167 fraction of SiH₄ to total flow), the H₂ flow was 200 sccm, and the combined flow of PH₃ and SiH₄ was 40 sccm. The PH₃ was supplied in pure SiH₄ at 20% and 0.01% concentrations. The range of PH₃ concentrations shown in the figure was achieved by mixing pure SiH₄ with one of the two available PH₃ sources. With the introduction of the PH₃ dopant gas, the compressive intrinsic stress increases to a maximum value at $\sim 10^{-4}$ [PH₃]/[PH₃]+[SiH₄]. As the PH₃ concentration is further increased, the compressive stress drops drastically to a value well below the RHP intrinsic a-Si:H value. The dotted line through the 10% PH₃ point acknowledges that this film may contain enough phosphorous to measurably affect the mechanical parameters of the film and thus cause Eq. (4) to give an intrinsic film stress that departs somewhat from the actual intrinsic stress present in the film.

FIGURE 33. Intrinsic stress of a-Si:H films deposited at 400°C as a function of concentration of phosphine in the gas phase. The films were deposited in the RHP system with gas flows as follows: 200 sccm H₂ and a combined flow of 40 sccm PH₃ and SiH₄.

It is interesting to note that the deposition conditions which produce the highest intrinsic compressive stress for each deposition technique as shown in Fig. 2 are the same conditions which produce the best electronic-grade a-Si:H films by each of the deposition techniques.^{2,12} Features of electronic-grade a-Si:H include low defect densities ($< 10^{16} \text{ cm}^{-3}$) and an Urbach edge with a slope of $\sim 50 \text{ meV}$. While these optimized electrical properties are achieved at a deposition temperature of 250°C in

a GD system, they are obtained at 400°C in an RHP reactor. In addition, a-Si:H films deposited by RHP at 400°C are more stable, with a lower saturated density of light-induced defects, than optimized GD films.¹²

It is expected that there should be a correlation between IR spectral characteristics and intrinsic stress in a-Si:H films. For example, it has been reported that Si-H induces compressive stress, whereas Si-H₂ bonds relieve compressive stress.^{13,14} Further investigation of the correlation between intrinsic stress and hydrogen incorporation in a-Si:H films is required.

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Fluorescence spectra of discolored EVA in solar cells treated at 85C for 198 days

Fig. 3. Fluorescence spectra for EVA A9918 films in encapsulated solar cells heated in oven in the dark and exposed to UV light (RS4 lamps) at 85°C for 198 days. Curve 1: Oven-heated, light yellow EVA; curve 2: RS4-exposed, yellow-brown EVA; and curve 3: RS4-exposed, brown EVA. Synchronous scans as in Fig. 1. The spectra were measured directly through the glass superstrate.

Fluorescence spectra of weathering-degraded EVA films [Ex. L = 370 nm]

Fig. 4. Fluorescence spectra for weathering-degraded films of (1) a light yellow-brown EVA A9918, (2) a yellow-brown EVA 15295, and (3) a dark brown EVA A9918 obtained at an excitation wavelength of 370 nm. The peak intensity in the 460-560 nm range was normalized to show the red shift of the emission peak as the discoloration increased

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