Comparison of the Electronic Properties of a-Si: H and a-Si:D Thin Films and Solar Cells

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The properties of a-Si:H and a-Si:D films and solar cells, prepared in a low-contamination CVD system are compared. While having essentially similar basic properties, the a-Si:D films show considerably higher stability under illumination, and faster thermal recovery of the degraded photoconductivity. Light-pulse treatment is effective in further increasing the stability of the films. In agreement, single-junction solar cells fabricated with an intrinsic a-Si:D layer show higher stability than a-Si:H cells.

1. INTRODUCTION

Hydrogenated amorphous silicon is one of the most promising materials for economic, efficient thin film solar cells. Presently, however, the performance is limited by the thermally reversible degradation of the photoconductivity under illumination, known as the Staebler-Wronski (SW) effect.[1,2] While large advances have been made in understanding the mechanisms involved, there has been little progress in preparing degradation-resistant films. Recently, we reported that treatment of intrinsic a-Si:H films by cycles of high-intensity light pulse irradiation and dark annealing results in an improvement in the light-stability.[3] It has also been recently reported by Matsuda and co-workers[4] that replacing hydrogen with deuterium reduces the SW effect in intrinsic films. In this work, we compare the properties, and in particular the light-induced degradation, of high-quality a-Si:H and a-Si:D films and solar cells. We also report the effect of light-pulse treatment on the a-Si:D films.

2. EXPERIMENTAL

Intrinsic (i) a-Si:H and a-Si:D films of ~900 nm thickness were deposited by rf glow discharge decomposition of pure SiH_4 or SiD_4 under similar conditions. The solar cells were single-junction glass/textured SnO_2/p i n/Ag structures, where the p, i and n layers were B-doped a-SiC:H, 500 nm thick i-a-Si:H or i-a-Si:D, and P-doped μc-Si:H, respectively. Films and cells were prepared at ~200°C in a new type of separate chamber CVD system, incorporating a cart-less substrate transporting system, which reduces the contamination of the i-layer from dopants by about one order of magnitude compared to a conventional separate chamber system.[5]

Light pulse/annealing treatment[3] was carried out under vacuum at 200°C by irradiation with 1 kW/cm^2 intensity Xe light pulses, using a treatment time of 90 min and pulse interval of 5 min. After treatment the films were annealed in the

Table 1. Properties of as-deposited and light-pulse treated films.

		H,D (at.%)	E_{opt} (eV)	ΔE (eV)	σ_{dk} $(10^{-11}$S/cm)	σ_{ph} $(10^{-5}$S/cm)	$E_o{}^a$ (meV)
a-Si:H	untreated	13	1.75	0.97	0.5	3.1	47
	pulse			0.84	3.4	1.9	
a-Si:D	untreated	16	1.80	0.93	0.9	2.7	47
	pulse			0.90	1.2	1.9	

[a]Urbach energy, measured by CPM.

dark at $\geq$150°C for more than 90 min. Light-induced changes were measured at 30°C under 100 mW/cm^2 simulated AM1 illumination.

3. RESULTS AND DISCUSSION

Table 1 compares the bonded H and D content, optical bandgap (E_{opt}), activation energy of the dark conductivity (ΔE), dark conductivity (σ_{dk}), photoconductivity (σ_{ph}) and Urbach energy (E_o) of as-deposited and light-pulse treated a-Si:H and a-Si:D films. The a-Si:D films have a photo- to dark conductivity ratio of more than 10^6, and generally fairly similar properties to those of a-Si:H. The deposition conditions used were optimised for a-Si:H, so that the slightly lower σ_{ph} of the a-Si:D films may be due to some non-optimisation. The large activation energies observed are typical of films prepared in the low-contamination CVD system. These films have lower densities of mid-gap and tail states compared to films prepared in conventional chambers. Light-pulse treatment results in a decrease in both ΔE and σ_{ph}, as a result of the creation of mid-gap states. The effect of the treatment on the properties of the a-Si:D films is smaller than for a-Si:H.

Figure 1 shows the changes of σ_{ph} with time under illumination for typical as-deposited and light-pulse treated films.
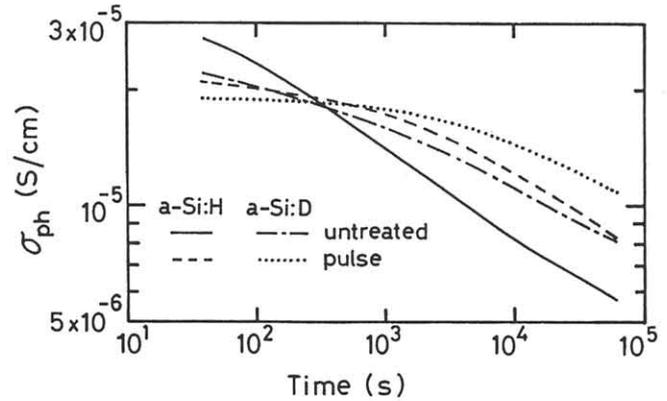
Fig.1. Light-induced changes of photoconductivity for as-deposited and light-pulse treated a-Si:H and a-Si:D films.

The as-deposited a-Si:D films have a lower rate of degradation, with a slope of -0.17, compared to -0.23 for a-Si:H. Although the initial σ_{ph} of the a-Si:D films is smaller, the value after 17 h is considerably higher than that of a-Si:H. Light-pulse treated a-Si:D films show even larger stability, with only a 40% decrease in σ_{ph} after 17 h. However, the degree of enhancement of the stability is not as great as for a-Si:H.

Thermal recovery of the degraded films was measured at 70-140°C. Figure 2 shows the recovery of σ_{ph} as a function of annealing time at 70°C. The a-Si:D film recovers at a faster rate compared to a-Si:H, with slopes of 0.29 and 0.15, respectively. Plots of time of recovery to
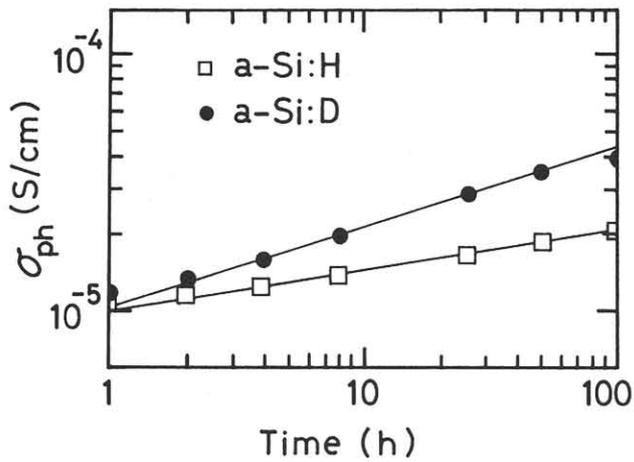
Fig.2. Thermal recovery of photo-conductivity for a-Si:H and a-Si:D films, measured at 70°C.
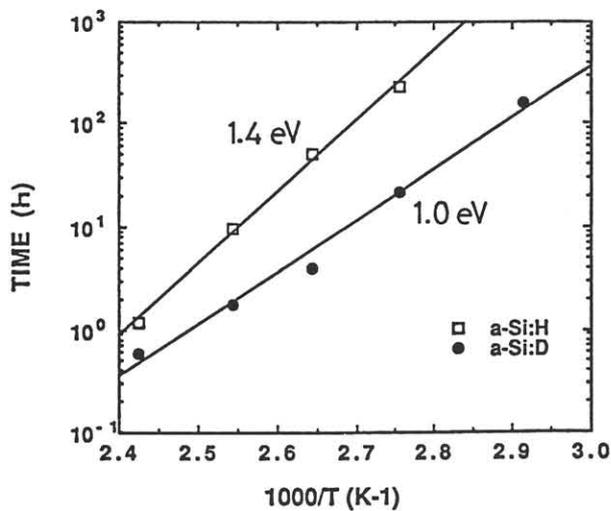
Fig.3. Thermal recovery time of photo-conductivity as a function of annealing temperature for a-Si:H and a-Si:D films.

the fully annealed σ_{ph} value against reciprocal temperature for a-Si:H and a-Si:D films are shown in Figure 3. The calculated activation energy for a-Si:H is 1.4 eV, which is close to the value expected for thermal annealing of the SW effect.[2,6] In contrast, a-Si:D has a smaller activation energy of 1.0 eV.

Figure 4 compares the light-induced changes of performance for solar cells
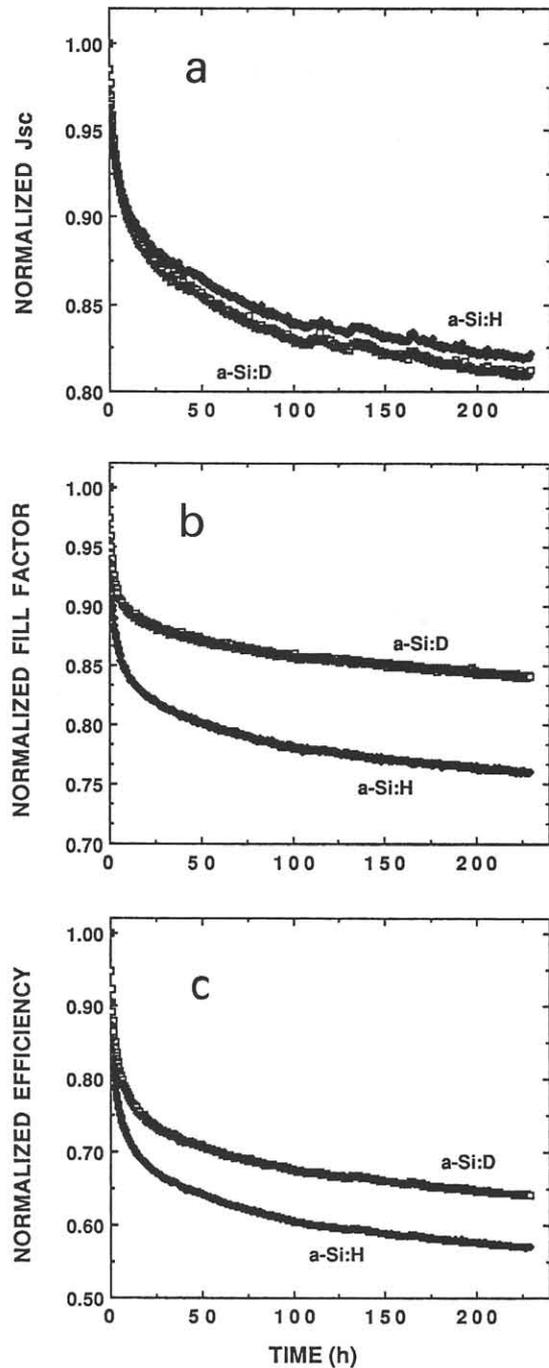
Fig.4. Normalised light-induced changes of (a) short-circuit current, (b) fill factor and (c) efficiency for solar cells with a-Si:H or a-Si:D i-layers.

prepared with a-Si:H or a-Si:D i-layers. The initial properties of the cells were J_{sc} = 17.4 and 16.8 mA/cm^2, V_{oc} = 0.93 and 0.95 V, FF = 0.68 and 0.63, η = 10.9 and 10.1%, respectively. Again, the lower conversion efficiency of the a-Si:D cells may be due to some non-optimisation of the deposition conditions. The a-Si:D cells show considerably higher stability of the fill factor, although slightly higher degradation of J_{sc} occurs. As a result, the efficiency of the a-Si:D cells degrades at a much slower rate than a-Si:H, so that the absolute efficiency is ca. 5 % higher after 120 h illumination.

Our results show, in agreement with those of Matsuda et al.[4] that a-Si:D exhibits a lower light-induced degradation of photoconductivity than a-Si:H. In contrast, the density of mid-gap states measured by CPM or ESR has been found to increase at a similar rate for both a-Si:D and a-Si:H under illumination.[4,7] It has been suggested[4] that this is due to the creation of two types of light-induced defect, one of which has a higher cross-section for electron capture and is created more readily in a-Si:H. The differences in behaviour under illumination, annealing and with light-pulse treatment seen upon substitution of hydrogen by deuterium imply that hydrogen is directly involved in these processes in a-Si:H films. It is, however, also possible that the effect may be due to subtle structural differences occurring during film growth caused by the isotopic substitution, although the film properties measured in this work appear to be very similar.

4. CONCLUSIONS

High-quality films of i-a-Si:D show considerably lower light-induced degradation of the photoconductivity and faster thermal recovery than a-Si:H, while having generally similar physical and electronic properties. The films can be further stabilised by treatment with cycles of high-intensity light pulse illumination and annealing. Substitution of the i-layer by a-Si:D in single-junction solar cells, having an initial efficiency of <10%, also results in a large increase in the light-stability.

6. REFERENCES

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