

Recent advances in understanding of a-Si:H based materials and performance of their solar cells

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A brief review is presented of some recent results which shed new light on the nature of gap states and the microstructure of high quality a-Si:H materials which can be directly related to improved performance and stability of their solar cells. These results demonstrate that charged, and not just the neutral dangling bond D° , defects have to be included in assessing the quality and stability of a-Si:H for solar cells. It is also shown that the commonly used measurements and their interpretation, solely in terms of neutral dangling bonds and their densities, are inadequate and measurements are discussed which allow the contributions of charged defect states to be evaluated. Recent results are also presented and discussed in which the effects of hydrogen dilution on the growth and microstructure of a-Si:H materials have been characterised using real-time spectroscopic ellipsometry. Guided by the derived deposition phase diagram for these materials, systematic studies could be carried out on p-i-n solar cell structures which have provided insights into the properties of these materials and a systematic approach for improving performance and stability of their solar cells.

Keywords: amorphous silicon, solar cells, stability, gap states, protocrystallinity.

1. Introduction

Continuous progress has been made in improving the performance and stability of a-Si:H solar cells based primarily on empirical approaches. However, further progress over current stabilised efficiencies has been seriously limited by the lack of detailed understanding of a-Si:H properties directly related to the performance and stability of their solar cells. This has in part been due to the absence of reliable quantitative correlations between materials and their solar cells as well as those between the growth and microstructure of a-Si:H based materials and the performance and stability of their solar cells. Recently, however, progress has been made in both these areas and this paper reviews some of the recent work on protocrystalline a-Si:H materials and their solar cells [1,2] as well as on the reliable correlation between properties of materials and their solar cells [3–5] which illustrate this.

Protocrystalline a-Si:H is material which is prepared close to but not at the amorphous-microcrystalline phase boundary [1,2,6] and exhibit excellent solar cell properties and stability. The film thickness at which the amorphous→microcrystalline transition occurs is however a function of the hydrogen dilution gas flow ratio ($R = H_2/SiH_4$). Recently RTSE has been used to characterise the evolution with thickness of the microstructure, opti-

cal properties, and degree of ordering in a-Si:H films deposited with different R. The identified regimes of film thickness and R within which a-Si:H and μ c-Si:H phases are present are then used to obtain an evolutionary phase diagram for Si:H film deposition. Guided by such a phase diagram, systematic studies were carried out on p-i-n solar cell structures in which the dilution of the i-layers in the cell structures and their thicknesses were changed [7], so that the contributions to the fill factors of both the protocrystalline and the transition region could be identified and evaluated.

The absence of direct correlations between material and cells that is essential for systematically improving solar cell materials can in large part be attributed to the inadequacy of the commonly used approaches to characterising the materials. These have focused on the evaluation of the densities of neutral dangling bonds $N(D^{\circ})$ [8] and are based on the assumption that the nature of degradation kinetics is the same for all materials as well as their solar cells [9,10]. Although it has been suggested that defects other than the neutral dangling bonds, D° , determine the properties of a-Si:H materials and solar cells [5,11] their contributions, particularly to the light induced changes, have in general been neglected. This paper presents results obtained on a-Si:H solar cell materials fabricated under different deposition conditions which identify some of the important effects that the charged defects have on materials and solar cells and point to approaches that can be taken to characterise them.

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2. Protocrystalline a-Si:H materials and solar cells

The distinguishing characteristics of protocrystallinity, a term used to describe a-Si:H prepared close to the microcrystalline phase boundary in deposition parameter space [1,2], are their improved stability under illumination and the appearance of AM1.5 degraded steady states after illumination for approximately 100 hours [12]. Of key importance to solar cell performance is the transition region between the amorphous and microcrystalline regimes in deposition parameter space, where a low concentration of small crystallites is likely to be present in the material. The electronic properties of such a transition region could be characterised using a-Si:H p-i-n structures where the thicknesses of the i-layers, produced with hydrogen dilution levels $R = H_2/SiH_4$ as high as 20, were guided by an evolutionary deposition phase diagram obtained from RTSE. The properties of intrinsic protocrystalline materials and their transition to microcrystallinity with increasing thickness were investigated by characterising the cells in the annealed state as well as with AM1.5 illumination until they reached a degraded steady state.

The evolutionary phase diagram separating the deposition of a-Si:H (left) and μ c-Si:H (right) thin films as a function of layer thickness D_b and H_2 dilution ratio R on a-Si:H ($R = 0$) substrates is illustrated in Fig. 1. The onset of the microcrystalline phase can be identified from a well-defined increase in surface roughness layer thickness accompanied by a change in optical properties during growth as observed with RTSE [1]. The inset illustrates a p-i-n structure whose i-layer exhibits a transition from the amorphous phase to the microcrystalline phase with increasing thickness. Because the transition between the two

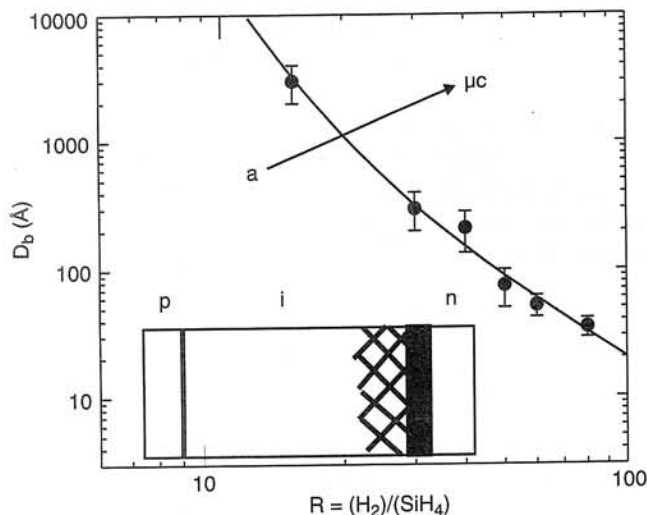


Fig. 1. Evolutionary phase boundary (solid line) separating the deposition of a-Si:H and μ c-Si:H as a function of the layer thickness d_b and H_2 dilution ratio R on an a-Si:H ($R = 0$) substrate. The inset illustrates the transition (crosshatched region) from amorphous (left) to microcrystalline Si (right) in the intrinsic layer of the p-i-n cell.

phases is not expected to be abrupt, a crosshatched region is also included. The thickness at which the onset of microcrystallinity occurs depends on R ; as a result, it was possible to tailor the cell structures so as to probe the contributions of the three regions shown in the inset of Fig. 1. The thicknesses of the cells were selected on the basis of the observed onsets of microcrystallinity illustrated in Fig. 1, where the thicknesses at which the onsets occur are ~ 1000 Å, ~ 3000 Å and > 5000 Å for $R = 20, 15,$ and $10,$ respectively.

Insights into the protocrystalline materials and the onset of the amorphous-to-microcrystalline phase transition region were obtained primarily from the fill factors (FF) of the different cell structures. The range of i-layer thickness over which FF is determined solely by the i-layer bulk was established from results on p-i-n cells with the same p-layer and p/i interface and $R = 10$ i-layers from 1100 Å to $10,000$ Å. Results obtained with p-i($R = 10$)-n cell structures are shown in Fig. 2. Here a systematic increase can be seen in the annealed state FF with the decrease in i-layer thickness to 1800 Å, indicating that these FF values are not limited by the contacts. Corresponding changes occur with thickness in the degraded steady state FF which extend to thickness less than 1800 Å, but the effect of the contacts for these very thin cells cannot be discounted. Because the open circuit voltages in these cells are particularly sensitive to light induced defects in the p/i interface region [12], their observed stability (within 5–10 mV) indicates that the influence of such defects is negligible.

The effects of changing R from 0 to 20 were investigated using cells having 3300 Å thick i-layers. The stabilised fill factor values for these cells increase as R increases from 0 to 10 and then remain constant from $R = 10$ to 20. For $R \leq 10$, the FF in the annealed state remains constant but then significantly decreases for $R > 10$. These observed decreases are not related to any adverse effects at the p/i interface region since insertion of a 200 Å $R = 20$ p/i interface region into cells having $R = 10$ bulk i-layers leads to

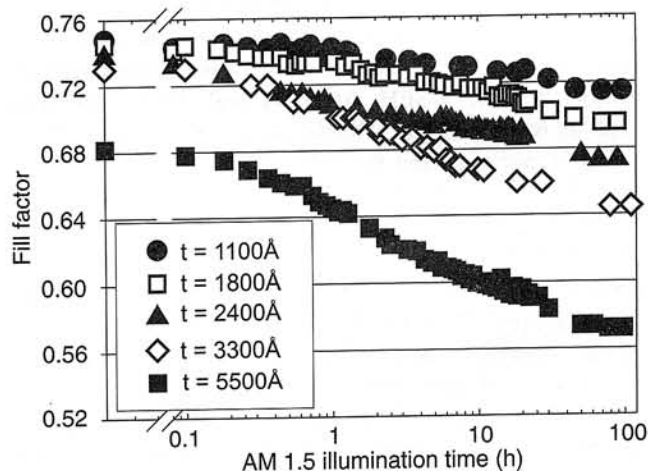


Fig. 2. Degradation of Si:H ($R = 10$) p-i-n cells with different thickness intrinsic layers under AM1.5 illumination at 25°C .

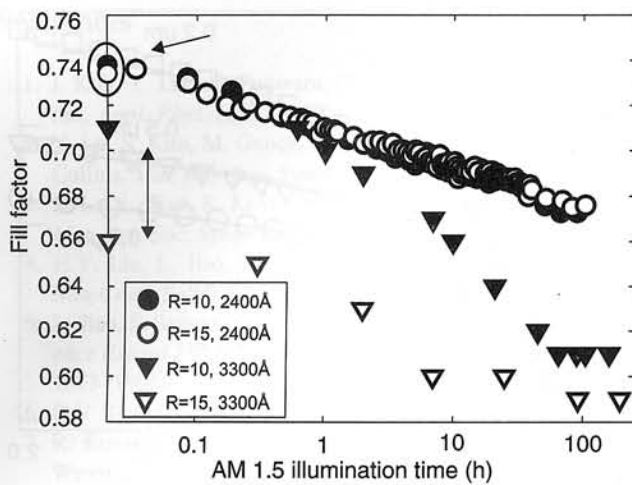


Fig. 3. AM1.5 25°C degradation of 2400 Å and 3300 Å p-i-n cells prepared with R = 10 and R = 15.

improved open circuit voltages in both the initial and degraded steady state [11]. However, based on the deposition phase diagram in Fig.1, such decreases in annealed state FF can be attributed to the onset of the microcrystalline phase in the 3300 Å thick i-layers. This is confirmed by results on cells with R from 10 to 20 having i-layer thickness ≤ 3300 Å. As the thickness of the i-layer decreases, and hence the contribution from the microcrystalline material nearest the n-type contact also decreases, the values of the annealed state FF for R = 15 and R = 20 i-layers approach the values for the corresponding R = 10 cells. The effect of this phase transition on the solar cell properties are illustrated in Fig. 3 with results on R = 10 and R = 15 i-layers. In Fig. 3 both the 2400 Å cells which have i-layers that are amorphous over the entire thickness have identical initial fill factors as well as AM1.5 degradation kinetics. However, the 3300 Å cell with R = 15, which spans the amorphous to microcrystalline transition, has an initial fill factor significantly lower than the 3300 Å thick R = 10 cell whose i-layer is amorphous throughout. Although the 3300 Å R = 15 cell has a lower initial fill factor than the R = 10 cell of equivalent thickness, the R = 15 cell degrades less.

3. Gap states in a-Si:H based materials

There has been a striking lack of meaningful correlations between a-Si:H thin film properties and those of the corresponding solar cells, particularly after light induced degradation. Because of the premise that the degradation phenomena in both films and cells can be explained by a single parameter (namely the density of neutral dangling bond defects, D^0), the characterisation of the a-Si:H materials has focused on this parameter with photoconductivity and CPM [8] measurements with their interpretations precluding any significant contribution from other defects. The results presented and discussed here however clearly demonstrate the importance of charged defects and indicate an ap-

proach for obtaining "operational parameters" of all the states in the gap that can be applied in the modelling of a-Si:H based solar cells. These results, which are obtained on a-Si:H materials fabricated with and without hydrogen dilution in different research laboratories, are from an approach for characterising gap states which has been previously described [12]. It is based on the detailed measurements of electron mobility-lifetime ($\mu\tau$) products (rather than just photoconductivity) and subgap absorption $\alpha(h\nu)$ over a wide range of carrier generation rates (G) using dual beam photoconductivity. In parallel, characterisation is also carried out on Schottky barrier cell structures, whose properties can be directly related to the intrinsic bulk material. The results obtained for films and Schottky barrier characteristics, in both the annealed and degraded states, are then self-consistently analysed using the subgap absorption model [12] and AMPS respectively [3]. Operational parameters for all the gap states were obtained from self-consistent fits using a five Gaussian distribution of gap states [12].

The contribution of charged defects to photoconductivity and subgap absorption characteristics become quite apparent when these properties are characterised in such detail. Their presence in the annealed state of the a-Si:H is clearly indicated by the large differences in both the magnitude of that the electron mobility lifetime, $\mu\tau$, products as well as their dependence on the carrier generation rates (G); these differences are much larger than those in the magnitude of the corresponding subgap absorptions, $\alpha(h\nu)$, and densities of neutral dangling bonds [13]. In the annealed state, there are also significant differences in the shape of subgap absorption spectra that are indicative of different distributions of gap states above and below midgap such as those associated with charged defects. Light induced changes in those types of defects are clearly indicated by the large, rapid decreases in the $\mu\tau$ products while there are no corresponding changes in $\alpha(h\nu)$ and hence $N(D^0)$ [14]. The extensively studied long term light induced changes in both the magnitude and dependence on G of $\mu\tau$ products are inconsistent with carrier recombination determined solely by $N(D^0)$ as are the light induced degradation kinetics which do not proceed with a $t^{-0.33}$ dependence predicted from such recombination [9]. Time dependencies similar to this are found only in undiluted a-Si:H films and then only at high generation rates. This is illustrated in Fig. 4 where the $\mu\tau$ products, at $G = 10^{19}$ $\text{cm}^{-3}\text{s}^{-1}$, are shown as a function of 1 sun illumination time for two undiluted (R = 0) and two diluted (R = 10) films together with lines indicating $t^{-0.3}$ and $t^{-0.2}$ as a guide to the eye. The time dependence close to $t^{-0.2}$ of the diluted films clearly indicates an evolution of light induced recombination centers, which is distinctly different to that in the undiluted ones. The creation of defects, other than dangling bonds is further indicated by the differences in the time dependence observed with changes in the generation rates used to measure the $\mu\tau$ products (photoconductivity). The

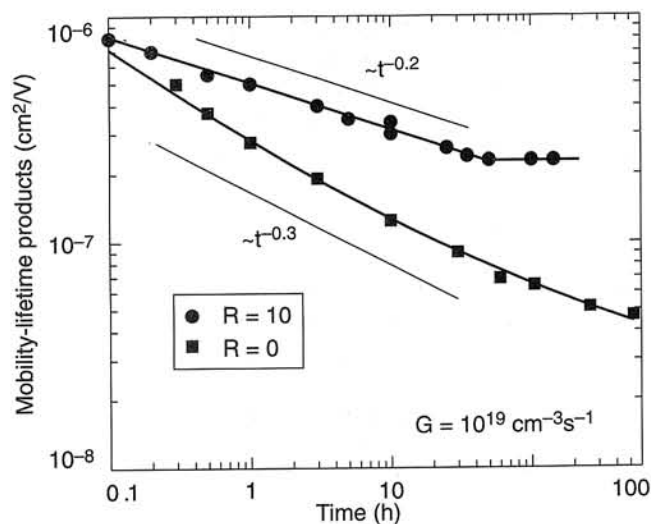


Fig. 4. Electron mobility-lifetime products, at $G = 10^{19} \text{cm}^{-3} \text{s}^{-1}$, as a function of 1sun illumination time for $R = 0$ and $R = 10$ films. The lines indicate $t^{-0.3}$ and $t^{-0.2}$ as a guide to the eye.

wide range of kinetics, such as shown in Fig. 4 requires the presence of defect states that are located closer to the band edges. Also, it is very important to note here that the absence of such a universal $t^{-0.33}$ time dependence for light induced changes, clearly points out the inconsistencies associated with the common practice of using arbitrary exposure times to characterise the stability of different a-Si:H materials.

The contributions of the charged defects to subgap absorption are more subtle because with prolonged illumination the magnitude of $\alpha(h\nu)$ becomes more and more dominated by the large densities of D^0 states [15]. However, the differences in the shapes of $\alpha(h\nu)$, which are not as large as in the case of the annealed state, do indicate the differences in the defect densities away from midgap. As a consequence, materials after 1sun degradation can have virtually the same densities of D^0 defects, as measured with ESR and indicated by the $\alpha(1.2 \text{ eV})$ values, and yet have distinctly different photoconductivity and $\mu\tau$ product characteristics and the distinctly different fill factors in corresponding Schottky barrier cell structures. It has been found that reliable correlation of results on films with those on Schottky barrier cell structures can only be made when equivalent degraded states are present, for example when both reach their degraded steady states after 1 sun illumination [3,12]. Selfconsistent fitting of all detailed results could be obtained using the same distribution of gap states only if it includes positively and negatively charged defects located above and below midgap respectively. In such a case good fits are obtained to the $\mu\tau$ product and $\alpha(h\nu)$ results on films as well as to the corresponding dark I-V, light I-V and quantum efficiencies on corresponding Schottky barrier cell structures having different thicknesses. Example of such selfconsistent fitting using the same "operational" gap state parameters for a five Gaussian distribution [3,12] is illustrated in Fig. 5 for the forward

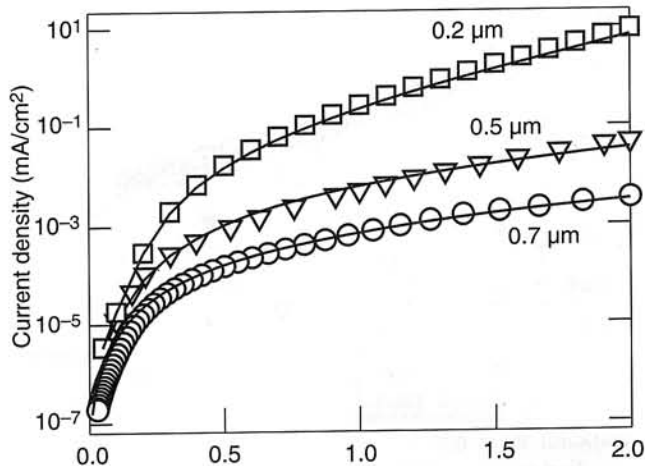


Fig. 5. Forward dark I-V characteristics of Schottky barrier cells with 0.2, 0.5, and 0.7 μm thick i-layers. Symbols are the experimental results and solid lines are the selfconsistent fits.

dark I-V characteristics of Schottky barrier cells having i-layers of 0.2, 0.5 and 0.7 μm thick. In Fig. 5, the symbols are the experimental results and the solid lines are the fits. Even though the distribution of gap states used here for neutral dangling bond and charged defects has allowed a wide range of results to be selfconsistently fitted, because of the many adjustable gap state parameters involved it cannot yet be considered to be unique.

4. Conclusion

The results of the studies reviewed here are an indicator of the improved understanding that is being achieved in the properties of a-Si:H materials and their effects on solar cell performance and stability. The advances made in identifying the role that charged defects have on the properties of the thin film materials are key to improving the methodologies for reliably evaluating and quantifying the stability of these materials. This and the selfconsistent analysis of detailed results on films and Schottky barrier cell structures that can yield "operational" parameters for all the gap states offers tools for a systematic approach to improving a-Si:H materials and solar cell structures.

New insights have also been obtained into the nature of protocrystalline materials and cells from recent studies on the transition from the amorphous to the microcrystalline phases as a function of the accumulated film thickness as well as their effect of this transition on p-i-n solar cell performance. Guided by a deposition phase diagram obtained from real-time spectroscopic ellipsometry the systematic studies, carried out on cell structures with i-layers deposited with different H_2 -dilution levels and thicknesses, allowed the effects of the transition from the amorphous to the microcrystalline phase within the Si:H layers to be identified. Thus for the first time it was possible to apply in a systematic way the properties of these structurally graded materials to the fabrication of efficient and stable solar cells.

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