DEFECT AND BAND GAP ENGINEERING OF AMORPHOUS SILICON SOLAR CELLS

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ABSTRACT

This paper demonstrates that the incorporation of an unoptimized, wide band gap a-SiC:H layer near the p-type emitter layer in addition to a graded bandgap "buffer" layer, leads to improved fill factors and open circuit voltages, in spite of the increased number of recombination sites at the p/i heterojunction. The *as deposited* efficiency as a function of a-SiC:H thickness shows an optimum of 10.5 % at a thickness of 10 - 20 Å. We have further improved this type of cell by incorporating a reverse carbon graded p-type layer and have thus achieved efficiencies in excess of 11.0 %. The cells are all amorphous and do not comprise antireflective coatings or enhanced back reflectors. A new defect engineering scheme to accomplish enhanced stabilized efficiencies of amorphous silicon solar cells is also proposed here.

INTRODUCTION

General Background

In amorphous silicon p^+-i-n^+ solar cells, the construction of the front 10 - 20 nm has a dominant influence on the overall performance. In 1981, a major improvement in the efficiency was obtained by incorporating a carbonated wide band gap p-layer, thus improving its window properties [1]. In 1986, the use of intentionally graded "buffer" p^+/i interfaces was reported to enhance the performance in the blue region of the spectrum [2]. Recently, the window properties of the p^+-layer have been further improved by using profiling schemes within the p^+-layer [3], and by employing oxygenated p^+-layers and buffer layers [4].

Researchers have speculated on the possible origins of the efficiency enhancement due to the p^+/i buffer layer. The most frequently found explanations range from the classical concept of relaxation of band gap discontinuity by reduced bond distortion to the modified boron diffusion profiles as a result of the buffer layer [2,5]. In general, the improved quantum efficiencies in the blue region, the higher open circuit voltage (V_{oc}) and fill factor values have usually been attributed to a reduced interface density of carrier recombination centers near the junction [2,6]. As pointed out recently [7], the reduced recombination losses can also be interpreted as due to the prevention of access to interfacial defects rather than to actual defect minimization.

New Solar Cell Optimization Approach

We have undertaken a new solar cell optimization scheme from the viewpoint of spatially separating electrons and holes at the p^+/i junction in order to prevent recombination, rather than merely minimizing the density of recombination sites. The new optimization scheme employed here involves the addition of a very thin unoptimized, wide band gap a-SiC:H layer near the p-type emitter layer in addition to the graded bandgap "buffer" layer. By employing this extra layer we intentionally *increase* the amount of defects at the p^+/i interface, which indeed is a counterintuitive approach when improved efficiencies are aimed at. We will show that this layer leads to *improved* fill factors and V_{oc}, whereas the diode quality factor (measured in the dark) shows an increase. These results will be substantiated by spectral response analysis and Secondary Ion Mass Spectrometry (SIMS) profiles.

In addition we have incorporated a bandgap grading scheme within the p^+-layer itself, leading to an efficiency in excess of 11 % without the use of microcrystalline layers or enhanced back reflectors. Finally, we suggest how the new insight in defect/band gap engineering schemes can be employed to the benefit of the stability of amorphous silicon solar cells.

EXPERIMENTAL

All devices were deposited in an ultrahigh vacuum multichamber PECVD system with a load lock and an automated transport chamber (PASTA) [8]. The 10 cm × 10 cm SiO_2/SnO_2:F coated glass substrates with a haze ratio of 20 % were supplied by Asahi Glass Company in Japan. All the semiconductor layers are amorphous and were deposited at low power and low temperature ($\leq$ 200 °C). Only conventional gases were used (SiH_4, CH_4, B_2H_6, and PH_3). Hydrogen is only involved as the carrier gas for doping gases. All grading schemes were achieved by linear gas flow variation or by abrupt gas flow shut-down without interruption of the plasma. The latter procedure leads to a compositional profile determined by the gas residence times inherent to the system. The back contact is a single layer of thermally evaporated silver.

The solar cell characteristics were measured using calibrated simulated AM1.5 global illumination (100 mW/cm^2) as defined by NREL (Golden, Colorado). The spectral quantum efficiency has been determined by phase sensitive detection of the response to low intensity monochromatic chopped light in the presence of white bias illumination at an intensity of about 100 mW/cm^2. Boron and carbon profiles have been determined by SIMS.

RESULTS & DISCUSSION

The initial basic structure in this study is a single junction glass/SiO_2/SnO_2:F/p-type a-SiC:H/graded buffer layer/a-Si:H/n-type a-Si:H/Ag cell with an efficiency of 9.5 %. Thus we start from a basic cell which already has a p^+/i buffer layer. The modification to this structure consists of a thin a-SiC:H layer ("insulator layer") which is inserted between the p^+-layer and the existing graded buffer layer. The deposition time of this insulator layer has been varied from 0 to 10 seconds. After this, a buffer layer is deposited by linearly decreasing the CH_4 flow.

Solar cell characteristics

Fig. 1 shows the open circuit voltage V_{oc}, the short circuit current density J_{sc}, the fill factor and the efficiency of the deposited solar cells as a function of insulator deposition time. It can be seen that V_{oc} is monotonously increasing, whereas J_{sc} and the fill factor show an optimum at about 5 to 7 seconds deposition time. The overall efficiency also shows an optimum of 10.49 % for this duration of insulator layer deposition.

The improved efficiency is accomplished in spite of the increased number of recombination sites at the p^+/i heterojunction brought about by the insulator layer. This layer, in addition to the buffer layer, due to its large band gap, serves to further reduce the back

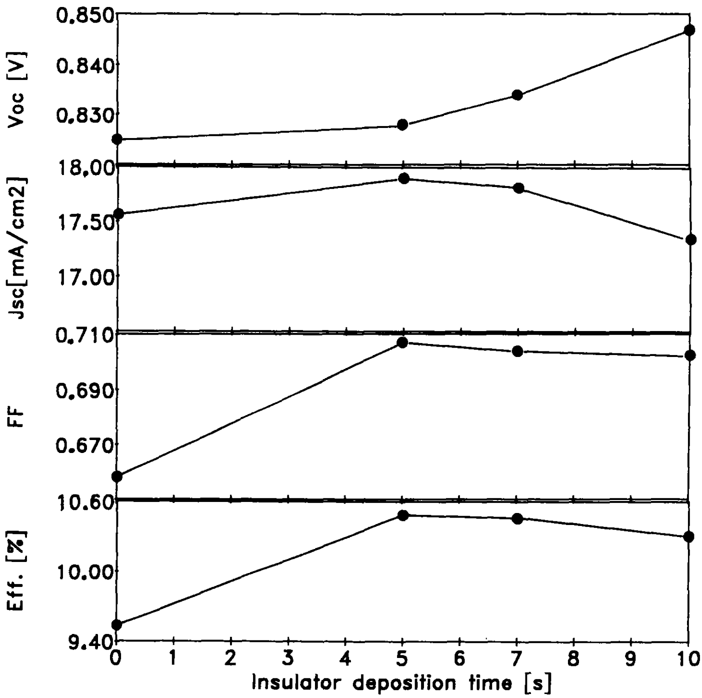

Figure 1: The open circuit voltage V_{oc}, the short circuit current density J_{sc}, the fill factor and the efficiency of single junction solar cells as a function of insulator deposition time.

diffusion of electrons generated near the p^+/i interface. Simultaneously, access of electrons and holes to the excess recombination sites is prevented as the a-SiC:H material in the insulator and the buffer has a lower effective mobility. The low mobility is caused by larger potential fluctuations of the band edges in the a-SiC:H alloy material, leading to increased trapping probability along with long recombination lifetimes [9].

Thus the extra a-SiC:H layer genuinely acts as an insulator layer, in that it spatially separates electrons and holes. With increasing thickness, the insulator layer introduces an internal series resistance which should lead to shallower *log* I versus V diode characteristics in the dark. Indeed, as shown in Fig. 2, the diode quality factor increases monotonously with the thickness of the insulator layer. Therefore, experimental evidence is obtained for the suggestion [7] that enhanced efficiencies can be obtained at *increased* values of the "ideality" factor n. Nevertheless, if the insulator layer becomes too thick, it may start acting as a barrier, leading to too high a series resistance.

The structures with optimized insulator/buffer combinations should exhibit a higher quantum collection efficiency in particular in the blue part of the spectrum, since these wavelengths are absorbed nearest to the p^+/i junction. In Fig. 3 we show the spectral quantum collection efficiency at 0 V for devices made with insulator layers of 0, 5 and 10 seconds duration. As expected, the systematic improvement in the spectra in the region of short wavelengths is clearly visible.

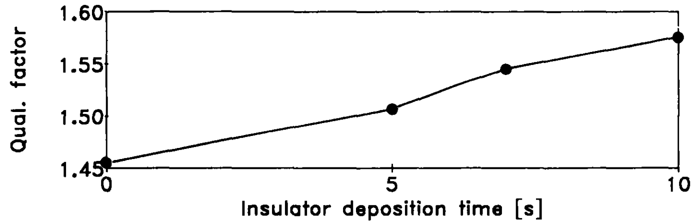

Figure 2: The diode quality factor n as a function of insulator deposition time.

Special Reverse Carbon Graded p$^+$-layers

Recently, a substantial improvement of the solar cell characteristics was reported [3] by replacing the conventional p-type window layer with a p-type carbon graded layer made with dimethylsilane and disilane. The carbon content was gradually increased away from TCO/p$^+$ interface.

We found that a similar beneficial effect can be obtained using the more conventional methane and silane gases (curve D in Fig. 3). In our grading scheme, the methane flow was linearly increased over the thickness of the p$^+$-layer from about 50 to 100 % of the homogeneous p$^+$-layers in the reference cells. This was followed by an insulator layer of 7 s and a buffer layer. As will be seen in the next subsection, the insulator layer is in fact a graded layer due to the natural decay time of B_2H_6 in the discharge; the newly constructed p$^+$-layer thus consists of three graded sublayers. As in ref. 3, the open circuit voltage and fill factor could be maintained for shorter deposition times for the first part of the p$^+$-layer. This leads to minimized optical losses in the p$^+$-layer and a substantially higher value for J_{sc} (Fig. 4) without a loss in V_{oc}.

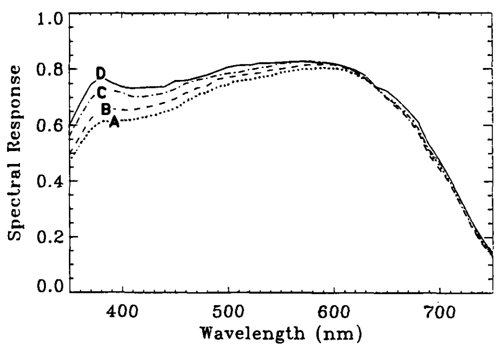

Figure 3: The spectral quantum collection efficiency for p$^+$-i-n$^+$ devices made using increasing insulator layer deposition times (curves A (0 s), B (5 s), and C (10 s); curve D has been obtained from a device incorporating a 7 s insulator layer and a special reverse carbon graded p$^+$-layer.

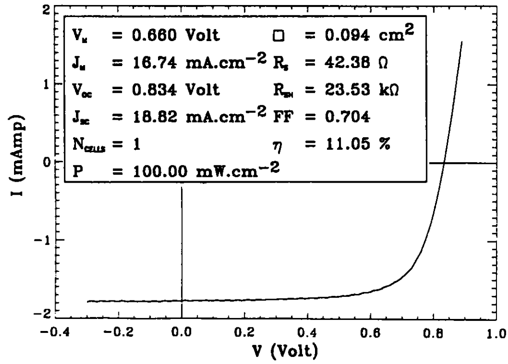

Figure 4: The I-V characteristics of the optimized cell in this study using standard AM1.5 global 100 mW/cm^2 illumination. This cell consists of a single all-amorphous p$^+$-i-n$^+$ junction without enhanced back reflector or antireflective coating.

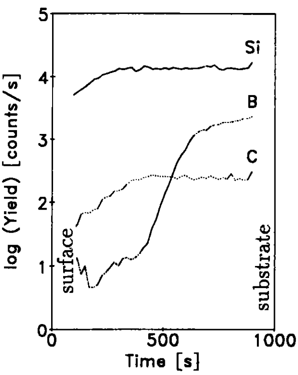

Figure 5: The SIMS yield profiles of Si, B, and C in a p-type a-Si:H layer showing a steep B step and a graded C profile, respectively, in the direction away from the substrate.

SIMS

The actual concentration profiles of boron and carbon in our films as a result of a number of characteristic gas flow manipulation schemes were determined by SIMS. In Fig. 5 we show, as an example, the B, C and Si relative profiles for a p-type a-SiC:H layer which was deposited using SiH_4, CH_4, and B_2H_6. First, after a certain deposition time, the B_2H_6 flow was switched off abruptly, and then, after some more time, the CH_4 flow was linearly ramped down to zero during 30 s. In spite of pumping speed limitations, the residence time is such that the B concentration in the film falls off at least as rapidly as 2.4 nm per decade, which is the depth resolution with the present SIMS set up (1.5 keV O_2^+). The C concentration, which was deliberately ramped down more slowly, showed a fall-off of 10 nm per decade. With the help of this analysis, we were able to design the triple graded p-layer more accurately. The total p-layer is 110 Å thick and consists of 80 Å of reverse carbon graded p-layer with a carbon content which is gradually increased up to 8 at.-% and a boron content of less than 1 at.-%, followed by 18 Å of boron graded layer with high carbon concentration (insulator layer), and 12 Å of carbon graded near-intrinsic layer (buffer layer).

Stability

We propose that the present defect/band gap engineering concept can be utilized to accomplish enhanced stabilized efficiencies of amorphous silicon solar cells. For instance, the stabilized efficiency should barely be affected if less stable material is placed into a region of high electric field. In principle, the space charge built up in light-induced defects could even enhance the stabilized efficiency by spreading the electric field such that it extends deeper into the i-layer.

If direct non-radiative recombination does provide the mechanism for defect creation, then a region of high susceptibility to the Staebler-Wronski effect incorporated at a small distance from the interface should lead to a more uniform creation of defects. This was experimentally achieved by increasing the deposition rate away from the interface and then decreasing it again. Indeed it was found that the efficiency degradation was less for a device with a profiled i-layer compared to a device with a constant i-layer. Whereas the fill factor for blue light after light soaking was only 0.498 in the reference device, it amounted to 0.553 in the device with the profiled i-layer. We will elaborate on this in a forthcoming publication.

CONCLUSIONS

We have undertaken a new solar cell optimization scheme from the viewpoint of spatially separating electrons and holes at the p^+/i junction in order to prevent recombination, rather than merely minimizing the density of recombination sites. This approach has been combined with the concept of grading the p-layer itself.

The devices were deposited in a UHV multichamber system (PASTA). SIMS analysis has shown that compositional changes within 10 - 20 Å required for p^+/i junction optimization can indeed be achieved without plasma interruption in this system. The final optimized structure for the single junction amorphous silicon solar cell is this study is glass/SiO_2/SnO_2:F/reverse carbon graded p-type a-SiC:H/ a-SiC:H insulator layer/carbon graded buffer layer/intrinsic a-Si:H/ n-type a-Si:H/Ag, with an efficiency in excess of 11 %.

This work therefore provides experimental evidence for the suggestion [7] that enhanced efficiencies can be obtained at an *increased* concentration of junction recombination centers, consistent with the increased values of the "ideality" factor n.

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