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Electronic Characterization and Light-Induced Degradation in nc-Si:H Solar Cells

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ABSTRACT

The electronic properties of working nanocrystalline silicon (nc-Si:H) solar cell devices with conversion efficiencies up to 8.6% were studied using junction capacitance methods. The set of devices examined were deposited on both specular stainless steel substrates and Ag/ZnO textured back reflectors. These devices included nc-Si:H grown under constant H_2 dilution, and also with profiled H_2 dilution to control the crystallite sizes and volume fraction. Transient photocapacitance and transient photocurrent spectroscopies were used to obtain sub-band-gap optical spectra. A comparison of these two kinds of spectra also allowed us to deduce the minority carrier collection fractions as a function of temperature and light-induced degradation. Light-soaking was found to cause a distinct decrease in minority carrier collection, as well as a consistent *decrease* in defects responding to drive-level capacitance profiling. A tentative microscopic model is proposed that accounts for these degradation effects in nc-Si:H.

INTRODUCTION

Thin film microcrystalline silicon solar cell devices deposited by plasma enhanced CVD processes close to the amorphous phase boundary, usually termed "hydrogenated nanocrystalline silicon" (nc-Si:H), have improved markedly over the past couple years. At United Solar, cell efficiencies of single junction nc-Si:H devices are now approaching 9% [1], while triple junction devices employing a nc-Si:H bottom cell with an amorphous silicon (a-Si:H) top and silicon geranium (a-SiGe:H) middle cells now exceed the performance of the conventional a-Si:H/a-SiGe:H/a-SiGe:H triple junction devices [1]. The nc-Si:H films fabricated in this method are recognized to be mixed-phase materials containing up to 40% of Si in the amorphous phase [2]. together with crystallites of sizes roughly between 5 to 20 nm.

Recently we showed how the electronic properties of these materials could be characterized using junction capacitance methods [3]. For example, using transient photocapacitance (TPC) spectroscopy together with transient photocurrent (TPI) methods, optical transitions within the amorphous component of these mixed phase materials could be identified, and the relative collection efficiencies of the photo-generated majority *vs.* the minority carriers could be estimated. In this fashion, we also demonstrated that prolonged light-exposure in nc-Si:H caused a substantial decrease in the relative degree of minority carrier collection. Moreover, while it appears that this light-induced degradation arises from optical transitions across the a-Si:H component of this material [4], we could not observe any increase in the density of deep defects within the material as revealed by the sub-band-gap spectra.

Whereas our earlier studies primarily employed specialized a-Si:H/nc-Si:H/a-Si:H sandwich test device structures, the current study applies the same capacitance-based characterization methods to a series of actual working nc-Si:H n-i-p photovoltaic devices of varying efficiencies. Therefore, we could now attempt to correlate the results of our measurements with the actual device performance parameters. We have also been able to gain some additional insight into the fundamental nature of light-induced degradation in such nc-Si:H based photovoltaic devices.

Table I. Performance properties nc-Si:H devices examined in current study

Sample No	Substrate	J_{sc} (mA/cm^2)	V_{oc} (volts)	FF	Eff (%)	H_2 Dilution
14027	Ag/ZnO	26.5	0.469	0.581	7.22	Profiling
14036	SS	17.38	0.448	0.568	4.42	Profiling
14037	Ag/ZnO	25.99	0.429	0.512	5.71	Constant
14038	SS	17.36	0.451	0.531	4.16	Constant
13993	Ag/ZnO	24.39	0.548	0.641	8.57	Profiling

SAMPLES AND SAMPLE TREATMENT

Five sample n-i-p devices were deposited at United Solar Ovonic Corporation onto either specular stainless steel (SS), or textured Ag/ZnO substrates. The nc-Si:H intrinsic layers were deposited using a modified VHF glow discharge process with a thickness roughly 1.5 μm. ITO dots with an area of 0.05 cm^2 or 0.25 cm^2 were deposited on the p layer as top contacts. Three of the samples, as indicated in Table I, were grown using a H_2 dilution profiling process to control crystalline size and volume fraction distribution. Two comparison samples were grown using a constant H_2 dilution. The structures deposited onto textured substrates were nearly identical to actual end-product devices and so constituted material tested in its optimized geometry.

Substrate texturing enhances the spectral response of a device through light-trapping effects, especially in the longer wavelength regime. This is clearly beneficial to achieve the highest conversion efficiencies; however, texturing also significantly modifies the spectral response, yielding a somewhat distorted representation of the optical spectral response of the nc-Si:H film itself. Figure 1 illustrates this by comparing two transient photocurrent spectra for one textured substrate sample device (13993) with one without texturing (14036). We attribute the textured sample's flatter TPI response above roughly 1.3 eV, and its apparently broader Urbach energy below 1.1 eV to such light-trapping effects. The specular sample is thus expected to provide a much less distorted picture of the actual nc-Si:H optical absorption properties.

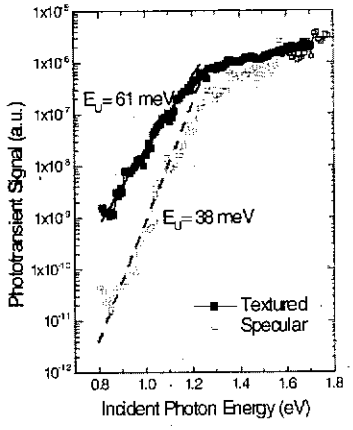
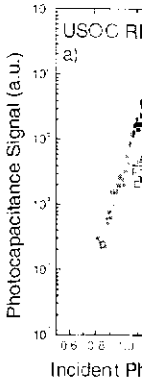


FIG 1. TPI spectra for samples on specular and textured substrates are aligned at the higher optical energies for comparison purposes. The flatter optical response for the textured substrate sample above 1.2eV, as well as its broader apparent Urbach tail, are attributed to the light-trapping effect due to the textured substrate. Thus, the spectrum for the device deposited on the specular SS substrate is believed to more accurately represent the optical absorption properties of the nc-Si:H layer itself.



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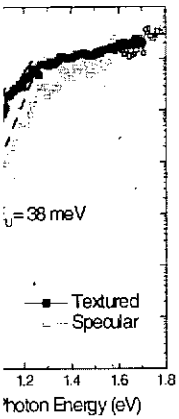


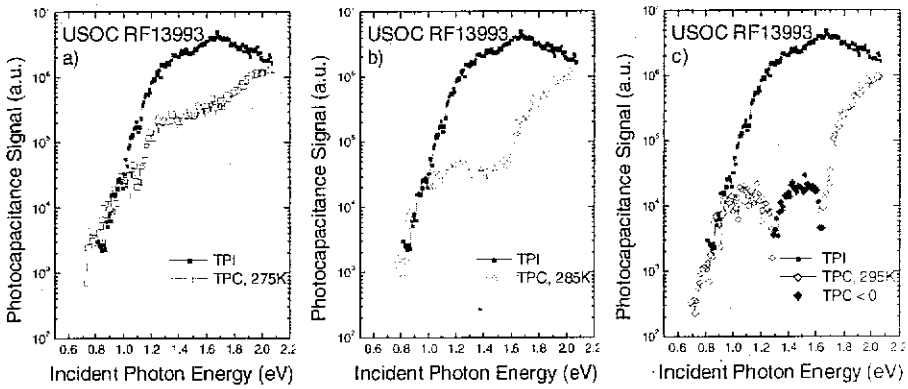


FIG 2. Comparison of TPI and TPC spectra at 275 K(a), 285 K(b), and 295 K(c) for the high-efficiency textured sample 13993. Nanocrystalline and amorphous phases are visible at low and high temperature, respectively. Note the negative TPC signal near 1.5 eV at 295 K.

TECHNIQUES AND RESULTS

The transient photocapacitance (TPC) and transient photocurrent (TPI) techniques have been described in detail elsewhere [5]. Both methods give results that closely resemble other types of sub-band-gap optical absorption spectra; however, they also incorporate important differences that reflect electrical properties of the materials being tested. Specifically, the TPC measurement returns a value that is proportional to the optically induced net change of charge within the depletion region. Thus, for an *n*-type semiconductor, the TPC signal is proportional to the *difference n-p*, where *n* is the number of electrons collected on the time-scale of the measurement, and *p* is the number of holes. The transient photocurrent signal, on the other hand, is proportional to the sum of *both charge carriers, n+p,* that leave the junction during the measurement. Thus, if during a measurement all holes become trapped in band-gap states and are unable to leave the junction, the TPC signal will be large and TPI will reflect the only the collection of the conduction electrons. For such single carrier processes, the ratio TPC/TPI will be constant, which we usually set to be unity. Ratios of TPC to TPI at incident photon energies where both types of carriers are being collected are then less than one and reflect the relative number of minority carriers collected compared to the majority carriers. This ability to deduce the minority carrier collection fraction is a unique feature of our spectroscopic methods.

Figure 2 displays 1.1 kHz TPC profiles for sample 13993 at three different temperatures. In each case, the TPC profile is aligned with the same TPI spectrum for reference. At 275 K and 285 K, we obtain TPC spectra that agree qualitatively well with spectra we obtained in previous work [3]. At 285 K the spectra clearly exhibit the amorphous phase present in these nanocrystalline devices by showing both a distinct a-Si:H bandtail below the amorphous silicon optical gap, as well as evidence of mid-gap states at lower incident photon energies. These spectra also exhibit the previously observed temperature variation in that, by decreasing the measurement temperature by 10 K (Fig. 2a), the TPC spectrum increases by more than a factor of 10 near 1.5 eV, indicating a corresponding decrease in the net hole collection at this photon energy. An even more dramatic change is observed when the temperature is raised to 295 K in this sample: the TPC signal actually becomes slightly *negative* near 1.5 eV. The absolute value of these negative data points are plotted in solid symbols in Fig. 2c. Such a negative signal shows

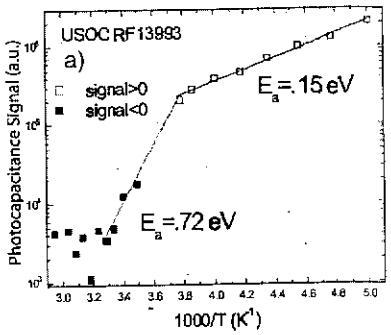


FIG 3. Variation of TPC signal with temperature at an optical energy near 1.5eV. A positive constant was added to the TPC signal to allow these data to be plotted on a logarithmic scale (the negative region is indicated by the solid symbols). We chose the constant that best extended the exponential dependence into the regime above 270K. This graph indicates thermally activated behavior for hole collection and, in contrast with previous results showing a single activation energy near 0.2eV, this sample reveals a second regime at higher temperatures with a significantly larger activation energy.

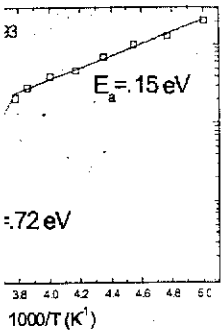
that *more* holes are being collected than electrons at these optical energies, indicating that some of the photo-excited electrons become deep trapped and cannot escape during the 500 ms time window of our measurement. However, at both larger and smaller optical energies, where the optical response of the amorphous silicon component plays a relatively increased role (with its poorer hole collection) the signal becomes positive again. Therefore, the slight negative response in this region is not in itself so important; rather, it simply reflects the fact that the hole collection in the nanocrystalline region is extremely good.

We examined the temperature dependence of the TPC signal in detail at an optical energy near 1.5 eV for this sample and found that the hole collection appeared to be thermally activated as shown in Fig. 3. At lower temperatures, when the hole collection was strongly suppressed, we obtained an activation energy for hole collection that was very similar to that found previously [3]. However, in the temperature regime above 270K, a significantly larger activation energy (near 0.72 eV) was exhibited. We tentatively attribute this to hole trapping into deep defects, possibly Si dangling bonds in the amorphous component. The fact that this deeper hole trapping accounts for only about 10% of the total (by comparing the magnitudes of hole collection at 200K and 300K) seems consistent with the idea that these deeper defects reside in the phase with the lesser volume fraction in these materials, that is, the amorphous phase.

We also found that the relative hole collection was strongly sample dependent. For the three textured samples: 13993, 14027, and 14037, we determined the relative hole collection fractions at 300 K by aligning TPC and TPI spectra in the defect regime at 0.9 eV and then determining the average TPC/TPI ratio near an incident optical energy of 1.5 eV. This provided an estimate of the ratio $(n-p)/(n+p)$, from which the ratio p/n of collected holes relative to electrons could be determined. For the three textured samples studied, there indeed appeared to be a good correlation between the n/p collection ratios determined in this fashion and the cell conversion efficiencies. However, a much larger number of samples will need to be examined in this fashion before taking this result too seriously.

LIGHT INDUCED DEGRADATION IN NANOCRYSTALLINE SILICON

Although nc-Si:H does not suffer as severely from light exposure as amorphous silicon, prolonged light soaking typically reduces the conversion efficiency by several percent [4]. Several of our samples were examined both in "State A", after a sample had been annealed for 1 hour at 450 K, as well as in "State B", a degraded state which we obtained by exposing the



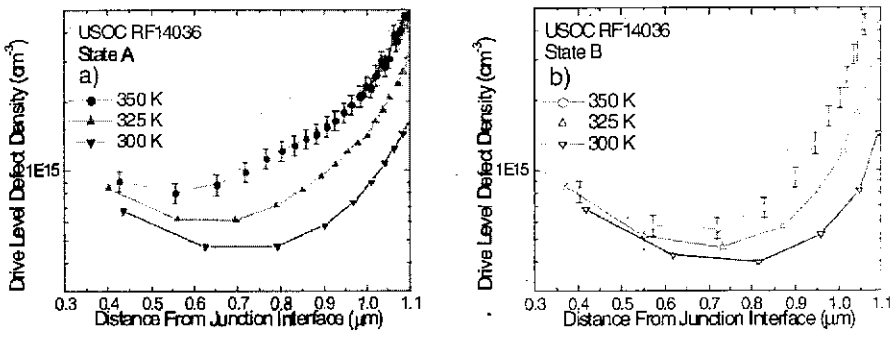


FIG 4. 1.1 kHz DLCP profiles obtained for a series of temperatures for both (a) the annealed State A and (b) light-soaked State B of one nc-Si:H sample deposited on specular stainless steel. The increasing density with temperature is due to the response of deep defects. However, this response from the deep defects actually appears to be reduced after light soaking. Representative errors bars are displayed for the 350K profiles in each graph.

sample to 20 hours of red-filtered light (>620 nm) from a tungsten-halogen source at an intensity of 400 mW/cm^2. Effects of such light soaking could be observed both in the photo-transient spectra as well as in drive-level capacitance profiles (DLCP).

Numerous studies of light-induced degradation in a-Si:H, using DLCP have clearly revealed a systematic increase in the density of deep defects, by factors varying from roughly 2 to almost 50.[6,7] However, our previous DLCP studies for nanocrystalline materials indicated almost no change [8]. In contrast, for some of the current series of nc-Si:H devices, particularly for samples 13993 and 14036, the DLCP measurements have revealed a significant deep defect response, as is illustrated in Fig. 4. This may partly be due to the smaller effective doping levels in these samples which enable us to more clearly observe the contribution from the deep defect. What is particularly surprising, however, is that when such a deep defect response is apparent, we consistently have found that it *decreased* after prolonged light exposure, as illustrated in Fig. 4b.

The effect of light soaking on the TPC spectra of sample 13993 is shown if Fig. 5. We see that the TPC signal changes appreciably. In particular, the negative signals near 1.5 eV become significantly positive in State B. This corresponds to a loss of hole collection by an even greater degree that that obtained by reducing the measurement temperature from 295 K to 275 K in State A (see Fig 2).

To reconcile these observed effects of light-soaking on the DLCP and TPC measurements, we tentatively propose a microscopic degradation model. First, we note that that DLCP density

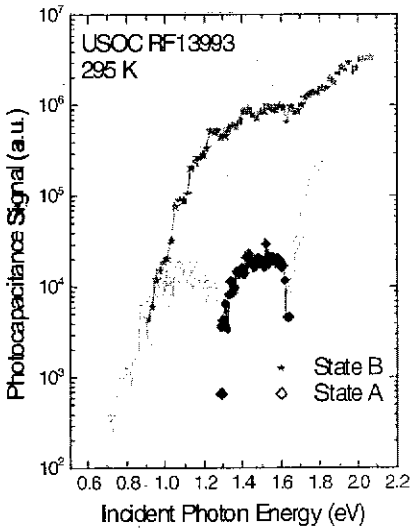


FIG 5. Comparison of the TPC spectra for sample 13993 before and after light-soaking.

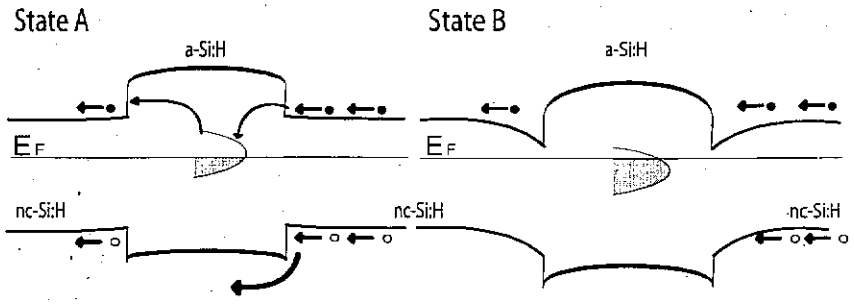


FIG 6. Schematic of a possible model to explain light-induced changes observed in the drive-level profiles and the photocapacitance spectra. In State B, defects have shifted down in energy with respect to the bulk conduction band and holes see a larger potential barrier at the phase boundary. In the scenario illustrated, positive charge has collected at the a-Si:H/crystallite interfaces, and is compensated by negative charge in the a-Si:H region, as well as in the crystallite nearby.

represents the integral over the density of states in the gap between the Fermi level and a thermal response energy. Thus, the observed decrease in drive level density may result from defects effectively "shifting out" of the energy region defined by our DLCP measurement parameters. Likewise, reduced hole collection implies an impediment to hole transport. Both of these observed effects might originate from a shift in the potential distribution between the nanocrystallites and amorphous regions of these mixed phase materials, as shown in Fig. 6. Such a shift in the relative potentials of the two phases could occur during light-soaking due to a separation of the photo-generated charges, with positive charge accumulating at the amorphous-nanocrystalline phase boundary, and compensating negative charge being added to the dangling bond defects within the amorphous regions. Future studies are underway to test some of the other implications of such a microscopic model.

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