CHARACTERIZATION OF THE SnO_2/p AND ZnO/p CONTACT RESISTANCE AND JUNCTION PROPERTIES IN a-Si p-i-n SOLAR CELLS AND MODULES

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ABSTRACT

A new method has been developed to characterize the TCO/p contact in a-Si p-i-n superstrate solar cells and modules. The method is applied to a series of devices fabricated at BP Solar on commercial SnO_2 and ZnO-coated SnO_2 having different p-layer recipes and pre-deposition treatments. Values of the contact resistance (R_C) of 1±0.5 -cm^2 were found for a wide range of TCO and p-layer processing including ZnO. Temperature dependence of R_C gave barrier height of 40-55 meV. Analysis of devices with a thin ZnO layer on SnO_2 and with different predeposition treatments indicates lower V_{oc} and FF observed with ZnO is not due to the contact but to changes in the p/i junction recombination. The solar cell performance is very sensitive to the ZnO surface treatment but R_C is not. No evidence was found for a blocking or high resistance ZnO/p contact.

INTRODUCTION

Transparent conductive oxides (TCO) are essential to the optical and electrical performance of a-Si based solar cells. For superstrate a-Si TCO/p-i-n solar cells, minimizing the resistance between the p-layer and TCO is a critical issue for the incorporation of new TCO materials like ZnO or alloys of Zn-In-O and Zn-Sn-O and new p-layers like µc-SiC or µc-SiO into devices. However, characterization of the TCO/p interface is difficult since it is in series with the dominant p-i-n junction. We present a method to characterize the TCO/p contact in a functioning TCO/p-i-n device using dark JV measurements from a row of devices on a single isolated TCO strip. This method is simpler experimentally than a similar one we recently described [1] but uses the same analysis. It is useful for understanding resistance losses in modules and for diagnosing how plasma processing affects the TCO and junction properties since the TCO/p contact and TCO sheet resistance in a completed device structure are obtained. A result of this work is that R_C of the TCO/p contact is relatively independent of significant differences in p-layer, TCO material, and TCO surface treatments.

SAMPLE FABRICATION AND ANALYSIS

The substrates studied here were textured SnO_2-coated glass made by Asahi Glass (Type U) or AFG (PVTCO). Some of the Asahi SnO_2 were coated with a ~15 nm layer of sputtered ZnO to protect the SnO_2 from plasma damage. Three pre-deposition treatments of the SnO_2 and ZnO/SnO_2 substrates were investigated. Single junction a-Si p-i-n layers were deposited by PECVD at BP Solarex with two different a-SiC p-layer recipes, p1 and p2. Each SnO_2 strip of width W~0.8 cm had an In-solder contact to the SnO_2 at one end, and 6 devices (labeled m=1-6) fabricated in a row [1]. Device areas were 0.27 cm^2. L is the distance along the TCO from the Ag contact to the m-th device, and L /W is the number of squares of TCO. Typically 2 rows of 6 devices were analyzed on each piece to establish repeatability.

In the dark, the circuit model for the total device consists of a junction diode in series with a resistance. The total series resistance of the m-th device (equation 1) is the sum of the junction dynamic resistance R_J, the TCO/p contact resistance $R_{TCO/p}$, and the series resistance through the TCO R_{TCO}. R_{SH} is the sheet resistance of the TCO in /sq.

$$R = dV/dJ = R_J + R_{TCO/P} + R_{TCO} \quad (1)$$

$$R_{TCO} = R_{SH} \times (L/W) \quad (2)$$

$$R_J = (AkT/q)/J \quad (3)$$

$$R_S = R_{TCO/p} + R_{TCO} \quad (4)$$

Each device in a given strip is assumed to have the same R_J and $R_{TCO/p}$. This has been verified experimentally [1]. In a given row as L increases, the series resistance of the TCO between the device and the SnO_2 contact increases. One term in equation 1 is inverse with J, and one term is proportional to L/W.

Plotting R vs 1/J will have an intercept of the series resistance R_S and slope AkT/q. Plotting R_S vs L/W will have an intercept of $R_{TCO/p}$ and a slope of R_{SH}.

RESULTS FOR DIFFERENT P-LAYERS AND SnO_2

Figure 1 shows dV/dJ from the dark JV curves for 5 devices on Asahi SnO_2 with p-layer recipe p2. They form a family of parallel lines, consistent with the model of a diode in series with a resistance (eq. 1). Their slopes give an A-factor of 1.7 (from equations 1 and 3), and their intercepts (R_S) increase with L/W. Figure 2 shows the linear relation between R_S and L/W for these devices and others having p-layer conditions p1 or p2 on Asahi SnO_2 or AFG SnO_2. The intercepts give $R_{TCO/p}$ ~0.5-0.9 -cm^2. The slopes give R_{SH} ~11 /sq for Asahi and ~14 /sq for AFG. These A factors and R_{SH} are consistent with independent measurements.

Measurements were made from 223 to 393 K on these devices. $R_{TCO/p}$ and R_{SH} were obtained as functions of temperature. R_{SH} was found to be independent of temperature in this range, as expected for a degenerate semiconductor like SnO_2. The activation energy E_A for the contact resistance is shown in Figure 3 for devices with the p2 p-layer. Very similar values of E_A for each SnO_2 were obtained with the p1 layer. E_A is assumed to be the barrier height of the SnO_2/p contact.

Values of $R_{TCO/p}$ ~1 -cm^2 have been reported by others [2,3] using special test structures (not p-i-n devices), consistent with these values. Barrier heights between SnO_2 and p-layers have not been previously reported. Values of 40-50 meV from Figure 3 are ~2kT indicating an Ohmic contact.

RESULTS FOR ZnO/p CONTACTS AND SURFACE TREATMENTS

It is commonly reported that ZnO or ZnO-coated SnO_2 gives lower V_{oc} and FF when used as a substrate for p-i-n cells [3-6]. To date there is no commercial source for ZnO/glass substrates. Benefits of ZnO include higher resistance to H_2 plasma damage and higher transparency [7]. Thin ZnO layers have been investigated to protect commercial SnO_2 from H_2 plasma damage [7-10] but typically this has resulted in poorer device performance [3-5]. The Julich group [4] concluded from the change in FF with growth rate of p-layer and its doping level that interaction of H_2 with the ZnO surface creates an accumulation layer in the ZnO which reduces the FF. They then inserted a µc-Si n-layer between ZnO and the p-layer which improved the FF but reduced the current. They showed using XPS [10] that growth of a-SiC:H(B) on ZnO formed Zn at the surface was removed by the H_2 plasma treatment. A µc-Si(B)/a-SiC:H(B)combination p-layer yielded both good FF and V_{oc}.

We fabricated devices on ZnO/SnO_2 bilayers consisting of Asahi SnO_2 with sputtered ZnO. Three pre-deposition substrate treatments at 200°C were investigated: bakeout in a low pressure of Ar for 30 minutes, for 15 hours, or for 30 minutes followed by a 3 minute H_2 plasma exposure to remove residual water vapor. The H_2 plasma condition would damage the SnO_2, primarily by decreasing the transmission through formation of a Sn layer. It is also known that ZnO is hygroscopic.

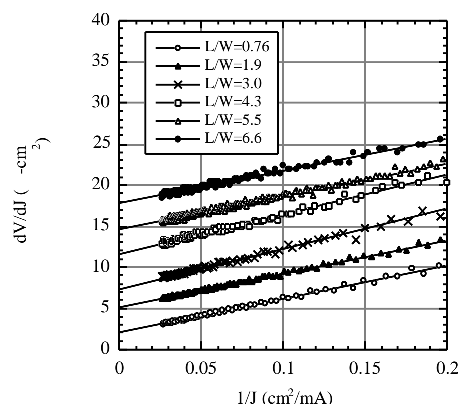

Figure 1. dV/dJ from dark JV for 6 devices on a strip of Asahi SnO_2.

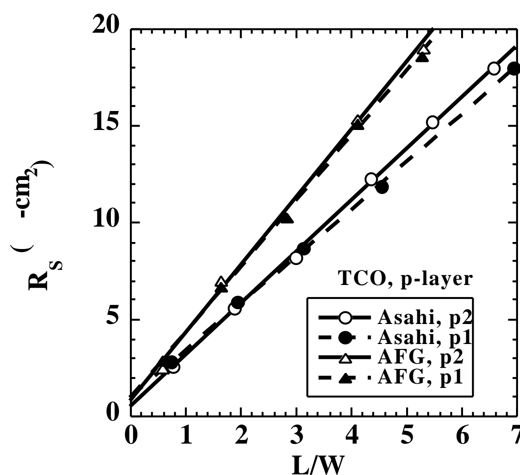

Figure 2. R_S vs L/W for 2 different p-layer recipes on AFG and Asahi SnO_2. The slope is R_{SH} and the intercept is R_C.

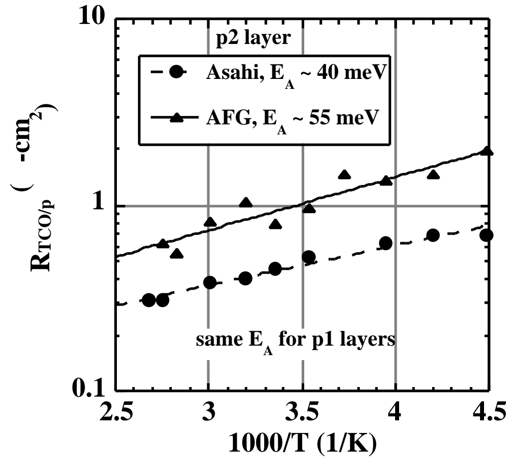

Figure 3. Arrhenius plot of R_C.

Table 1 lists the values of $R_{TCO/p}$ obtained from the analysis of the dark JV curves as described above (dV/dJ method) as well as from the method described previously [MRS method, ref. 1]. The good agreement verifies the present dV/dJ approach, which is simpler to implement. Also listed are the V_{oc}, J_{sc} and FF for the best device on each piece. Regarding the SnO_2 samples, there was little difference between 30 minute or 15 hour bakeout, but the 3 minute H_2 plasma degraded all parameters, presumably due to chemical interaction between the plasma and the SnO_2. Note that this resulted in the lowest J_{sc} and $R_{TCO/P}$, consistent with formation of a metallic Sn layer on the surface. The ZnO substrates had very low V_{oc} and FF with the 30 minute bakeout. Significant improvement in V_{oc} and somewhat less in FF occurred with the longer bakeout. FF continued to improve with the H_2 plasma treatment, opposite to the change in devices on the SnO_2 substrates. Note that J_{sc} decreases ~ 1 mA/cm^2 with the ZnO substrates in the H_2 plasma, suggesting the ZnO did not completely protect the underlying SnO_2 from damage, consistent with reports on different samples [6]. However, the crucial conclusion from Table 1 is that there was no significant difference in $R_{TCO/P}$ SnO_2 or ZnO substrates. The reason for poor V_{oc} and FF with ZnO must be found elsewhere.

Figure 4 shows log J vs [V-JxR_S] in the dark for the devices on ZnO/SnO_2 and SnO_2 with 30 minute or 15 hour bakeout from Table 1. The effect of R_s has been accounted for by the (JxR_S) term. The recombination currents J_O from the intercepts differ by 3 orders of magnitude (3E-9 and 4E-6 mA/cm^2) and the A-factors are 1.7 and 1.9 for the SnO_2 and ZnO/SnO_2 , respectively, with a 30 minute bakeout. With the 15 hour bakeout, J_O and A are unaffected for the SnO_2 devices (not shown), consistent with results in Table 1. On the ZnO/SnO_2 substrates, the longer bakeout decreases the forward recombination current around V_{oc} by 2-3 orders of magnitude but the data is no longer fit with a single exponential term. This figure indicates that the presence of ZnO and its surface condition has a major influence on the diode recombination, and that multiple (parallel) recombination paths can be present (multiple A factors). We speculate that the ZnO layer influences growth of the p-layer which in turn modifies p/i interface leading to different defect and recombination properties. It is well established that V_{oc} and FF are sensitive to the structure of the p/i interface of these devices.

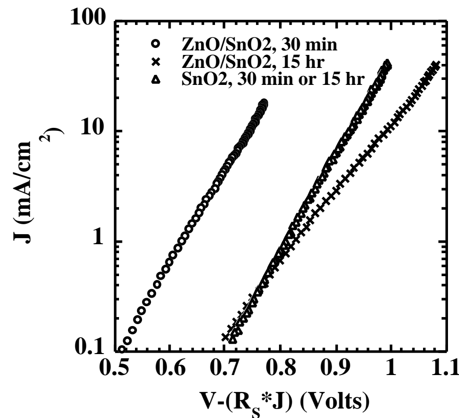

Figure 4. Log (J) vs V-[JxR_S] for a-Si devices on SnO_2 or ZnO/SnO_2 with 30 minute or 15 hour bakeout.

One of the JV characterization methods described in [1] allows direct measurement of the voltage across the TCO/p contact under forward bias current flow. A linear JV characteristic in this configuration indicates an ohmic contact. Any photovoltage between the TCO and p, which would oppose that of the dominant p-i-n junction, would also be detected by this method. We applied that method to these devices and found they all had ohmic TCO/p contacts without any photovoltage. This is confirmed with graphs of dV/dJ vs 1/J which are quite sensitive to detecting any current-limiting blocking. Figure 5 shows dV/dJ vs 1/Jfor three devices.

The a-Si devices are from Table 1 with SnO_2 and ZnO substrates having the 15 hour bakeout, and a CdS/CdTe device is shown which had a FF of 68%. They all have R_S ~ 4 -cm^2 from the intercept, and the CdTe device and a-Si device on SnO_2 have a factor of ~ 1.6-1.7 while the ZnO/SnO_2 device has A ~ 2.7 from the slope. The curvature at low values of 1/J for the CdS/CdTe device is a signature of a blocking contact [11], a well known problem in some CdTe devices due to a non-ohmic CdTe contact. Clearly there is no evidence of a blocking contact for the ZnO/SnO_2 device. Thus, the ZnO has a very similar R_C but much larger recombination current and non-ideal transport

compared to SnO_2.

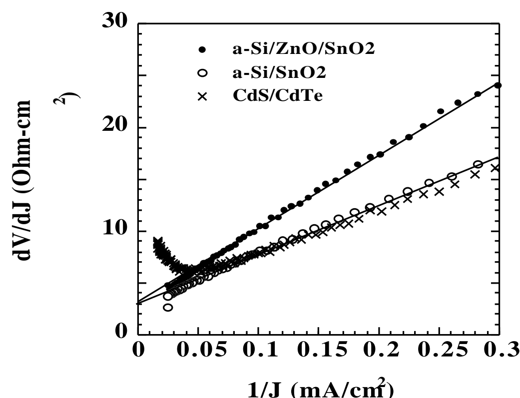

Figure 5. dV/dJ vs 1/J for a-Si on SnO_2, ZnO/SnO_2, and for CdS/CdTe devices. Curvature in data for CdTe indicates blocking contact.

Many groups use a value of the slope of the illuminated JV curve at open circuit (R_{OC}) as a measure of the series resistance to aid diagnosing low FF and other process changes. This correlation is only valid if the junction component has not changed. R_{OC} is given by eq. 1 evaluated at $J \sim J_{SC}$. This value is dominated by the junction component. Our results indicate that commonly observed increases in R_{OC} with ZnO are due to increases in A not R_S.

CONCLUSIONS

A new method has been presented to determine the TCO sheet resistance and TCO/p contact resistance in operating TCO/p-i-n superstrate devices. Contrary to conventional wisdom, the SnO_2/p and ZnO/p contacts are both ohmic, having low contact resistance of ~0.5-1.5 -cm^2. Activation energy for the SnO_2/p contact is only 40-50 meV. The "ZnO/p contact problem" is most likely due to changes in the growth of the p-layer resulting in a structurally and/or chemically different p/i causing increased recombination. No evidence for a blocking or high resistance ZnO/p contact was observed. This new technique can be helpful in evaluating new TCO materials or p-layer processings.

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Table 1. R_C from 2 methods for devices on SnO_2 and ZnO/SnO_2 with different pre-deposition treatments. Also shown are device performance. (a) dV/dJ method (here); (b) V_{AB} method (MRS)

TCO	Treatment(Ar bakeout or H_2 plasma)	(a) $R_{TCO/p}$ (-cm^2)	(b) $R_{TCO/p}$ (-cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)
Asahi	30 min Ar	1.3	1.0	0.89	13.3	70
ZnO/Asahi	30 min Ar	1.4	1.3	0.70	13.2	56
Asahi	15 hr Ar	0.8	0.6	0.90	12.5	71
ZnO/Asahi	15 0hr Ar	0.6	n/a	0.86	13.0	60
Asahi	30 min Ar then 3 min H_2 pl.,	0.4	0.3	0.79	9.3	58
ZnO/Asahi	30 min Ar then 3 min H_2 pl.,	1.3	n/a	0.83	12.0	64