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Improved fill factors in amorphous silicon solar cells on zinc oxide by insertion of a germanium layer to block impurity incorporation

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Amorphous silicon based solar cells deposited on zinc oxide (ZnO) exhibit reduced fill factor and open circuit voltage in comparison with tin oxide (SnO_2). One approach has been to use higher conductivity nanocrystalline layers to overcome the "higher contact resistance." Recent measurements have found the ZnO–p-layer contact resistance to be unchanged relative to SnO_2, while instead, the diode ideality factor is poorer on ZnO. We show that the insertion of a thin, amorphous germanium layer at the ZnO–p-layer interface improves the cell performance and diode ideality factor by suppression of oxygen and zinc incorporation in the silicon layers. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1773372]

The performance of hydrogenated amorphous silicon (a-Si:H) based solar cells is sensitive to the transparent conducting oxide (TCO) front contact.[1] Superstrate type, $p-i-n$ cells use a textured, SnO_2 front contact that is susceptible to reduction by hydrogen.[2–4] ZnO has been investigated as an alternative that is both resistant to hydrogen plasma induced darkening and has higher transmission.[5–7] However, fabrication of p-i-n type solar cells on ZnO results in a lower fill factor (FF) although higher short circuit currents are obtained.[7] It has been suggested that a rectifying contact is formed between the p-type a-Si:H and the n-type ZnO layer considering that a good contact is obtained between the n layer and the overlying ZnO layer that is used as part of the back contact.[8,9] There have been numerous attempts to overcome this problem including the fabrication of p-type ZnO.[10]

Another way to overcome the problem is to use a nanocrystalline silicon layer, which is significantly more conducting than an a-Si:H p layer.[8,11] While this is certainly suitable for nanocrystalline silicon solar cells, a-Si:H cells require an additional amorphous silicon carbon p layer to avert the formation of a microcrystalline silicon $p-i$ interface, which yields a significantly lower open circuit voltage. Additionally, nanocrystalline layers require long deposition times for nucleation and growth.[12]

Measurements of cells deposited on ZnO using two independent techniques have shown no signs of a rectifying barrier, and the contact resistance is comparable to that on SnO_2.[13] Instead, an increase of the diode ideality factor is consistently observed for cells fabricated on ZnO, suggesting enhanced recombination losses.[13] X-ray photoemission spectra reveal that the ratio of silicon oxide to silicon in p-layers deposited on ZnO are *higher* than that on SnO_2.[8] Germanium has been previously used as a barrier to oxide formation between silicon and an overgrown oxide layer,[14] which can be due to the preferred reactivity of oxygen with silicon over germanium.[15] Here, we report that using a thin, rapidly deposited germanium layer on ZnO improves the fill factor and open circuit voltage relative to standard (i.e., as grown on SnO_2) a-Si:H cells. This results in a reduction of the oxygen and zinc incorporated in the devices and correlates with an improvement in the diode ideality factor.

The glass –SnO_2($\sim$700 nm) or ZnO(700 nm)–p (10 nm)–i(250 nm)–n(30 nm)–ZnO(100 nm)–Al(200 nm) cells were fabricated using dc plasma decomposition of silane-hydrogen mixtures for the a-Si:H based p-i-n layers. Commerically available SnO_2 coated 3 mm thick, soda-lime glass, and atmospheric pressure chemical vapor deposited, fluorine-doped ZnO films on 1 mm thick specialty glass were used as superstrates.[16,17] The germanium layer was deposited using a plasma discharge ($\sim$50 mW/cm^2) with 30 to 1 hydrogen diluted germane for $\sim$4 s. Solar cells of $\sim$0.25 cm^2 were characterized using current–voltage as well as external quantum efficiency measurements. Each data point in the figures represents an average of at least 6 cells out of 36 cells deposited on each 8 cm × 8 cm glass superstrate. The data were statistically analyzed using JMP® software (SAS Institute Inc.) and the vertical nonoverlap of the diamonds indicates 97% certainty that the data sets are different. The TCO–p-layer contact resistance and TCO sheet resistance were obtained as the intercept and slope of a plot of the series resistance of cells along a TCO strip as a function of their distance from a common contact, as described in detail elsewhere.[13] The oxygen contents were measured using secondary ion mass spectrometry (SIMS).

In Fig. 1(a) we have plotted the measured transmission of a thicker germanium layer as well as the computed transmission of the layer actually used at the ZnO–p-layer interface. There is $\sim$2% transmission loss in the blue region and

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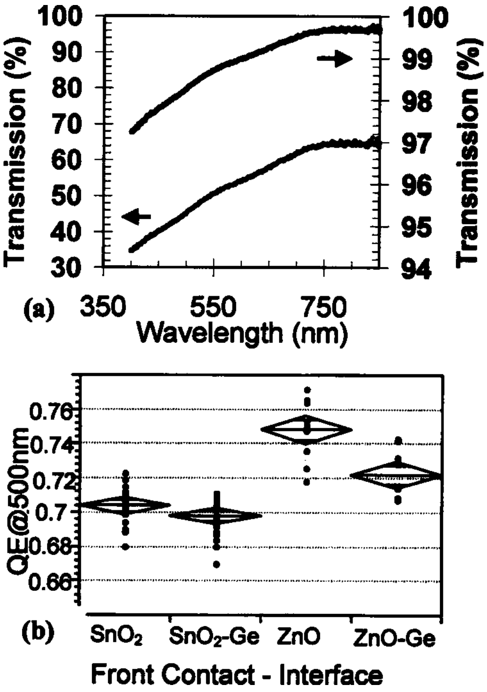

FIG. 1. (a) Measured transmission of a germanium layer comprising 25 $\times 4$ s depositions (lower line) and the calculated transmission for one 4 s deposition (upper line); (b) Average external quantum efficiency of *a*-Si:H solar cells deposited on SnO_2 and ZnO_2, with and without a germanium layer at the interface.

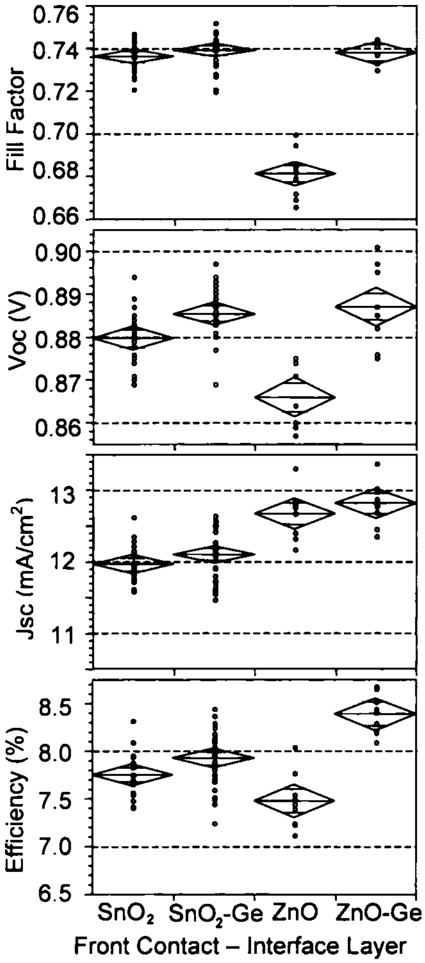

FIG. 2. Fill factor, open circuit voltage (V_{oc}), short circuit current (J_{sc}), and efficiency of solar cells deposited on SnO_2 and ZnO, with and without a germanium layer at the interface.

less at longer wavelengths due to the germanium layer, but the measurement is not refractive index matched to the device and therefore the losses could be $<2\%$ in the actual device. Figure 1(b) shows the external quantum efficiency using light of wavelength 500 nm for devices fabricated with and without the germanium interface layer on SnO_2 and ZnO coated glass superstrates. While the response decreases about 4% for cells on the ZnO superstrates, the drop is only about 1% on SnO_2. This smaller decrease for devices on SnO_2 is consistent with the germanium layer acting as a barrier to atomic hydrogen induced darkening of SnO_2 during deposition of the *p*-layer. Despite its narrow band gap and high defect density, the thin, rapidly deposited germanium layer appears to form an optically transparent contact layer.

Figure 2 shows all the photovoltaic (PV) parameters of the same cells shown in Fig. 1(b). While the changes in all the PV parameters due to insertion of the germanium interface layer are small and not statistically significant for cells fabricated on SnO_2, there are significant improvements in all parameters, except the short circuit current (J_{sc}), for devices on ZnO. The lack of change in (J_{sc}) due to insertion of the germanium layer on ZnO despite the changes in response at shorter wavelengths suggests that the high refractive index germanium layer alters optical coupling of the device as a whole. Table I shows values of the diode ideality factor, the TCO sheet resistance, and the TCO–*p*-layer contact resistance for diodes on SnO_2 and ZnO with the without the germanium layer at the interface. In agreement with earlier data,[13] the TCO–*p*-layer contact resistances are similar to those measured on other TCO–*p*-layer combinations, and are not altered by the germanium layer at the interface. The diode ideality factor, *A*, on the other hand, is significantly higher for the ZnO–*p*-layer interface compared to the SnO_2–*p*-layer interface, again in agreement with previous data.[13] Apparent values of $A>2$ indicate multiple forward current conduction mechanisms. Compared to the other three devices, the $J-V$ curve of the ZnO device in Table I have a different shape, leading to lower FF and a voltage-dependent *A* factor. However, insertion of the germanium layer at the ZnO–*p*-layer interface significantly reduces *A* which implies reduced recombination and elimination of other forward current mechanisms.

Figure 3(a) shows oxygen and tin profiles in devices fabricated with and without the germanium layer before deposition of the *p* layer on smooth SnO_2 coated glass while Fig. 3(b) shows the oxygen and zinc profiles in those on smooth ZnO coated glass. A comparison of the profiles shows that the interface appears broadened on the SnO_2

TABLE I. Diode ideality factor (A), TCO sheet resistance (*R* sheet), and its contact resistance (R_c) with the *p*-layer and the average fill factor for *a*-Si:H devices deposited on ZnO or SnO_2 with and without a germanium layer at the interface. Values of *A* were obtained between 2 and 40 mA/cm^2 forward bias and were voltage dependent for the device on ZnO.

TCO Interface	*A*	*R* sheet ($\Omega/\square$)	$R_c(\Omega)$	FF
SnO_2	1.63	11.6	1.7	0.736
SnO_2–Ge	1.61	12.8	1.3	0.739
ZnO	2–3	9.9	1.9	0.680
ZnO–Ge	1.73	10.2	2.2	0.737

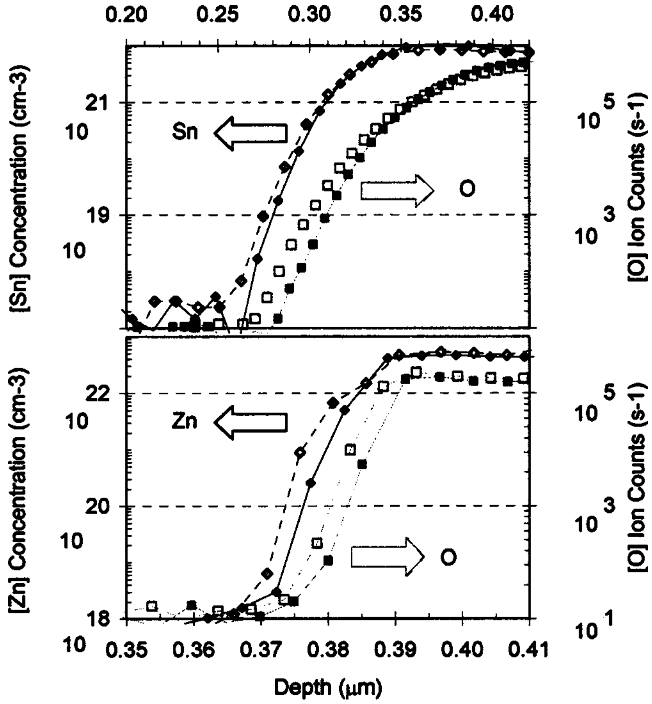

FIG. 3. Secondary ion mass spectrometric profiles obtained on *a*-Si:H solar cells with (closed symbols) and without (open symbols) a germanium layer on (a) SnO_2 coated superstrates–Sn (diamonds) and oxygen (squares), and (b) ZnO coated superstrates–Zn (diamonds) and oxygen (squares).

coated glass, which is a consequence of the commercially available "smooth" SnO_2 coated glass that has a 700 nm thick SnO_2 layer and is relatively rougher than the 100 nm thick sputter deposited ZnO coating used for the SIMS profiles. Tailing of both oxygen and zinc/tin into the silicon layers is observably suppressed in the sample that has a germanium layer at the interface. The ratio of oxygen with and without the germanium layer is larger on ZnO, indicating greater reduction of ZnO compared to SnO_2. The germanium layer is deposited rapidly and allows less time for reduction of the oxide by hydrogen,[11] while the lower reactivity of germanium with oxygen reduces oxygen incorporation in this layer.[14] Since the Zn atoms left on the surface tend to vaporize,[8] they are probably incorporated more readily than Sn atoms, which remain on the surface and cause the observed loss in transmission.

In summary, we have shown that a rapidly deposited, thin germanium layer can significantly improve the performance of *a*-Si:H solar cells deposited on zinc oxide. The improvement can be attributed to (1) the rapid deposition, allowing less reduction of the oxide, and (2) the lower reactivity of germanium with oxygen, which results in reduced oxygen contamination. This appears to reduce impurity induced recombination losses in the solar cell.

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