INTERFACE ENGINEERING BY USING GERMANIUM CARBON LAYER AT THE TCO/P INTERFACE IN SILICON THIN FILM SOLAR CELLS

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ABSTRACT: We present a method based on using germanium carbon alloy as the TCO/p interfacial layer to enhance the performance of the silicon thin film solar cells and modules. The presence of the germanium carbon interfacial layer can minimize the potential barrier as well as the depletion width, which contribute to the improvement of FF and V_{oc}; meanwhile, the loss in J_{sc} by previous methods can be eliminated due to the low parasitic absorption and index matching effect of the GeC film. We demonstrate significant improvement of the FF and V_{oc} without loss in J_{sc}. The efficiency is enhanced by 7% for a-Si solar cell and the result is also successfully applied to the large area production of a-Si and a-Si/μc-Si modules.
Keywords: TCO/p interface, Thin film solar cell, germanium carbon alloy.

1 INTRODUCTION

Thin film solar cells are attractive because of their low manufacturing cost and large area production. However, to compete for the larger photovoltaic markets and drive the utilization of solar cells for grid parity, a significant increase in efficiency is urgently required. One aspect of the study attempts to control the collection and minimize the recombination at the interfaces between different layers that make up the device and, which are crucial for efficient charge transport and thus, the conversion efficiency [1, 2].

The interface between the TCO contact and the p-type window layer was widely recognized as one of the limiting factors because of the Schottky barrier formed at this region [3]. The microcrystalline p-type layer (p-μc-Si) and metals with high work function [4] have been proposed to reduce the potential barrier; however, their effects are limited due to additional parasitic absorption loss, contamination or impractical consideration of mass production. Solutions using amorphous germanium thin film were also presented to improve the carrier collection [5]. Although efforts to improve the fill factor (FF) were achieved, solar cells containing such a layer still suffer from pronounced loss in short circuit current (J_{sc}).

In this paper, we provide a method based on germanium carbon alloy (GeC) which promises to break the prevailing paradigm by combining both its electrical and optical properties. We show large improvement of FF and V_{oc} without loss in J_{sc} by using this layer and study the effect of the improvement. Furthermore, we demonstrate pronounced efficiency improvement of silicon based single junction and tandem thin film solar cells and modules.

2 EXPERIMENTAL

Aluminum doped ZnO (AZO) deposited by sputtering was used as the front contact in p-i-n silicon thin film solar cells. The thickness was 800 nm after HCl (0.5%) wet etching. p-a-SiC (12 nm)/i(300 nm)/n-Si(25 nm) were fabricated using 60 MHz Plasmon Enhanced Chemical Vapor Deposition (PECVD). After the deposition of p-i-n films, 250 nm Al was used as the back contact. The germanium (a-Ge) and germanium carbon (GeC) thin films were also deposited using the same chamber of PECVD prior to the p-a-SiC layer deposition. During the a-Ge and GeC layers deposition, the H_2/GeH_4 dilution ratio was 1:1 and the VHF power is 0.75 W/cm^2. Data of the a-Si/μc-Si modules came from author's previous work at Astronergy and, more details can be found from the paper [6]. Solar cells of ~1 cm^2 were characterized by using a solar simulator under simulated AM 1.5G sunlight as well as external quantum efficiency (EQE) measurement. Work functions of materials were measured using Kevin-Probe (KP technology), conductivity was measured with Keithley2400 and optical properties such as refractive index, extinction coefficient and band gap were measured and fitted using Spectroscopic Ellipsometer (J.A.Woollam.Co., Inc.).

3 RESULTS AND DISCUSSION

The p-i-n a-Si solar cells with and without a-Ge or GeC layers between the AZO/p-a-SiC interface were fabricated. The data within TABLE I shows that FF of the solar cell with GeC interfacial layer was successfully improved to 0.714, the same as that obtained by using a-Ge, while the FF of the solar cell without such layers was only 0.68. The reasons for the improvement as a result of using a-Ge were the suppression of oxygen and zinc incorporation in the silicon layers [5] or the reduction of the Schottky barrier. In the case of GeC, the improvement was attributed to the reduced series resistance (TABLE I), which fundamentally depends on the barrier and depletion region at the AZO and p-a-SiC interface; in other words, reducing the band offset at the interface makes it possible to obtain a better ohmic contact and consequently high FF.

TABLE I Performance of a-si solar cells with different buffers at AZO/p-a-sic interface

Buffer	FF (%)	Jsc (mA/cm^2)	Voc (mV)	Rs (Ω-cm^2)	Rsh (Ω-cm^2)
Without	68	14.75	860	19	712
With a-Ge	71.5	14.05	864	15	1108
With GeC	71.4	14.5	870	16.7	1051

3.1 Schottky Barrier and Depletion Width

It is known that the barrier height as well as the depletion width are extremely important for the carrier

transport, and therefore are crucial for the FF. In order to understand the role of GeC at the interface barrier and depletion width, the classical metal-semiconductor junction model is used to estimate the barrier height, which can be easily written as [8]:

$$\phi_b = q\chi_s + E_g - E_a - q\chi_{TCO}$$

The depletion width in the p layer region can be derived from the abrupt junction assumption:

$$W_d = \left(\frac{2\varepsilon(\phi_b - 2kT)}{q^2 N_s}\right)^{1/2}$$

Where χ_{TCO} is the electron affinity of AZO, χ_s, E_g, E_a, ε and N_s are the electron affinity, band gap, activation energy, permittivity and doping concentration of p-type layer.

TABLE II The estimated barrier height depletion width at the AZO/p interface

Contact materials	P-a-SiC	a-Ge	GeC
χ	3.7	4	4
E_g	2.0	0.98	1.18
E_a	0.5	0.49	0.59
σ_d	10^{-4}-10^{-5}	1.2×10^{-4}	1.2×10^{-5}
ϕ_b	0.8	0.09	0.19
N_s	3×10^{-8}	2.1×10^{18}	1.6×10^{18}
W_d	18	5	10

The unit of χ, E_g, E_a and are eV. The unit of ϕ_b is $(\Omega cm)^{-1}$ The unit of N_s is cm^{-3} and the unit of W_d is nm. Data of concentration is taken from ref 8, 9, 10.
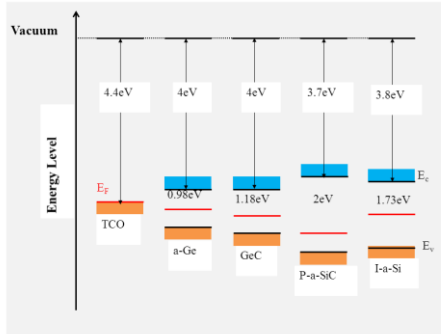

Fig.1. Energy levels of materials used in a-Si solar cells before equilibrium. Band gap of a-Ge, GeC, P-a-Si and i-a-Si layers are obtained from the Spectroscopic Ellipsometer measurement; the work function of AZO was measured using Kevin-Probe.

From Eq.1 and Eq.2, the barrier height and depletion width are determined by the work function and carrier concentration of the p-type layer. The values are shown in TABLE II. When there is no interfacial layer between AZO/p-a-SiC interface, the barrier height ϕ_b is estimated 0.8 eV and the width of depletion region W_d is 18 nm. Since the p-a-SiC layer of the device is only 12 nm, it is totally depleted. As the holes have to pass through this region, the high barrier height and wide depletion width will retard the holes transport. By contract, when a-Ge

buffer layer is inserted, the barrier height is largely reduced to 0.09 eV and the depletion width W_d is reduced to 5.7 nm. The extremely low barrier height and narrow depletion width are advantageous to holes transport; therefore, collection efficiency of the solar cell can be largely enhanced. For GeC, the barrier height is 0.19 eV and depletion width is 10nm respectively. Although the depletion width is larger than that of a-Ge, the barrier height is low enough that it is still sufficient to facilitate the holes transport where the transport through this region is dominated by the tunneling process.
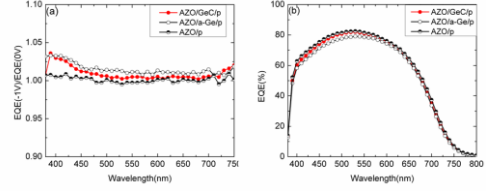

Fig 2. (a). The normalized EQE obtained by dividing the EQE with -1V bias by the EQE without bias; (b) the EQE of the solar cells with different AZO/p interfaces.

Confirmation of the role of the GeC layer in altering the AZO/p-a-SiC interfacial barrier and thereby influencing the internal electrical field can be found from the EQE measurement with reverse bias. The reverse bias was applied to enhance the electrical field of the device. Fig.2(a) shows the normalized EQE obtained by dividing the EQE with -1V bias by the EQE without bias. It can be seen clearly that when −1V bias was applied to the solar cell, significant increase of the EQE at the short wavelength was observed in the case of solar cells with a-Ge and GeC layers, the observation may be attributed to the different interfacial potential barrier. Since the applied reverse bias was partially used to compensate the potential barrier, the device with low barrier and narrow depletion width will have large EQE under the applied reverse bias. In addition to this, if the barrier is high and depletion width is wide, the voltage dropping on the interface will be high and consequently dropping on the intrinsic layer will be low. Therefore, the enhancement of the internal electrical field crossing the intrinsic layer is low and as a result, the improvement of the EQE (-1V) at long wavelength is intuitively expected to be small compared with that of the solar cells having low potential barrier and narrow depletion width

3.2 Parasitic Absorption

The J_{sc} in TABLE I was calculated from the EQE measurement shown in Fig.2 (b). The loss in J_{sc} was 0.7 mA/cm^2 when a-Ge was used; while the loss was reduced to 0.25 mA/cm^2 by using GeC (CH$_4$/GeH$_4$ flow ratio is 1:1). Fortunately, loss of J_{sc} could be minimized by continuing to increase the CH$_4$/GeH$_4$ ratio. The variation of the solar cell performance versus CH$_4$/GeH$_4$ ratio is shown in Fig.3, when CH$_4$/GeH$_4$ ratio is 4, A relatively improvement of 4.5% is obtained. In other words, in this condition, the loss in J_{sc} can be almost eliminated. We demonstrate the improvement of J_{sc} for the following reasons: the low absorption of GeC and the refractive index matching between AZO and a-Si layer.

In order to verify the above postulation, the a-Ge and GeC layers were prepared by varying the CH$_4$/GeH$_4$ ratio. Refractive index n and extinction coefficient k of

different layers were determined by Spectroscopic Ellipsometer measurement. As can be seen from Fig 4(a), germanium alloying with carbon has significant influence on the film optical properties. The refractive index and extinction coefficient decrease with increasing CH_4/GeH_4 ratio. Optical simulation using the transfer matrix method [11] was performed to understand the optical behavior of solar cells with different interfacial layers. The structure for optical simulation was the same as that of the fabricated solar cell except that the planar interface was assumed. Fig.4 (b) shows the absorption in a-Ge and GeC layers. Significant parasitic absorption is found in the a-Ge layer; however, absorption can be minimized when GeC is used. Apparently, the reduction of parasitic absorption loss due to the lower absorption coefficient of the GeC layer is the main contribution to the improvement of J_{sc}. Another contribution is the refractive index matching effect. It can been seen from Fig.4(a) that the index of GeC layers can be tuned between the index of ZnO and a-Si, as a result, the reflection at this interface is reduced; however, for a-Ge layer, pronounced reflection occurs because of larger index of the a-Ge layer. This effect of index matching contributes only a small amount to the J_{sc} in our case. The absorptance in active layer is also shown in Fig.4 (b), we can see that the EQE of the solar cells can largely be improved by using GeC. When CH_4/GeH_4 is 4, the EQE of the solar cell is almost the same as that of the solar cell without interfacial layer at long wavelength. And as the simulation is based on the planar structure, the calculated J_{sc} is smaller than that of the real solar cell. Nonetheless, the trend is obvious and a relative improvement of 4.5% is observed, which is consistent with the result of EQE measurement.
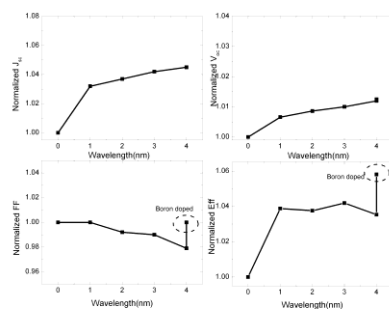

Fig 3. Variation of solar cell performance versus different CH_4/GeH_4 ratio.

3.3 Solar cell Optimization

Even though increasing the CH_4/GeH_4 ratio has the advantage of reducing the loss in J_{sc}, the FF reduces due to the decrease in the conductivity following the increase of carbon ratio in the GeC layer (Fig.3). In order to overcome the reduction of FF, boron doped GeC is chosen for further optimization of the conductivity of GeC, and as a result, FF with 0.715 was obtained again.

In addition to the gain in FF, the GeC layer also provides a contribution to the improvement of V_{oc} (Fig.3), which may also be a benefit gained from the improved interface contact. The solar cell with GeC exhibits a relative enhancement of 7%. The result was applied to a large area (1.1 m x 1.3 m) production of a-Si and a-Si/μc-Si modules. The initial power can be improved from 128 W to 133 W for a-Si and from 155 W to 158 W for a-

Si/μc-Si respectively. For a-Si/μc-Si tandem solar cells, from EQE measurement (not shown here) there is no J_{sc} loss in the top cell, but the loss in the bottom cell is obvious to observe. However, this can be solved by slightly increasing the thickness of the bottom cell.
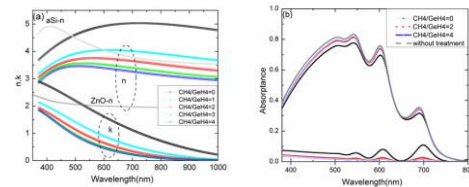

Fig 4. (a). The refractive index and extinction coefficient of a-Ge and GeC thin films; (b) The parasitic absorption in Ge and GeC layer and absorption in active layer.

4 CONCLUSION

In summary, it has been shown that the work function mismatch between AZO/p-a-SiC layer can be solved by using the GeC interfacial layer. The reduced barrier height as well as depletion width contribute to the improvement of FF (5.2%) and V_{oc} (2%), and low absorption and low refractive index GeC layer contributes to the enhancement of the J_{sc}. A relative efficiency enhancement of 7% is obtained for a-Si solar cell. The result is also successfully applied to a large area production of a-Si and a-Si/μc-Si modules and a significant increase of P_{max} is achieved.

5 REFERENCES

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