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Reflectance Improvement by Thermal Annealing of Sputtered Ag/ZnO Back Reflectors in a-Si:H Thin Film Silicon Solar Cells

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ABSTRACT

Silver can be used as the back contact and reflector in thin film silicon solar cells. When deposited on textured substrates, silver films often exhibit reduced reflectance due to absorption losses by the excitation of surface plasmon resonances. We show that thermal annealing of the silver back reflector increases its reflectance drastically. The process is performed at low temperature (150°C) to allow the use of plastic sheets such as polyethylene naphthalate and increases the efficiency of single junction amorphous solar cells dramatically. We present the best result obtained on a flexible substrate: a cell with 9.9% initial efficiency and 15.82 mA/cm^2 in short circuit current is realized in n-i-p configuration.

INTRODUCTION

Interest in thin film silicon solar cells has increased strongly in the last few years. Their development promises to help to produce abundant, low cost electricity at a time when mankind faces the challenge to move to alternative energy production processes. The low carrier lifetime in amorphous and microcrystalline silicon materials results in the need to reduce the thickness of the solar cells' active layer to well below the absorption length of light in the red part of the spectrum. Textured interfaces are used to scatter light within the solar cells to lengthen the light path and increase the generated photocurrent [1, 2, 3]. The n-i-p process is interesting because it can be used to produce light-weight, flexible and unbreakable modules, since the cell layers can be deposited on opaque substrates such as steel or on plastic sheets. The back contact and reflector in the n-i-p configuration is often realized by using metals having a high reflectivity like silver. Unfortunately, as the substrate itself needs to be rough to increase the light trapping, the silver layer has to be deposited onto a nano textured surface. In contrast to a silver layer deposited onto a flat surface, for which low parasitic absorptions are observed, silver deposited onto a rough substrate leads to parasitic absorption losses that take place within the metallic layer by the excitation of surface plasmon polaritons (SPPs) [4]. SPPs are known to be stronger when the metal quality is low [5]. In this contribution it will be shown that a proper thermal annealing of the silver layer leads to a large improvement of the film reflectance. The annealing is carried out at a moderate temperature, which allows the use of plastic substrates like polyethylene naphthalate (PEN). When the back reflectors are inserted into cells, the cell performance is improved significantly. In the first part, we present the effect of annealing on the bare reflectors, consisting only of the structured substrates and a silver layer. In the second part, the effect of annealing in the device is shown. By measuring the external quantum efficiency (EQE), and the total absorption of the whole cell we find a significant reduction in parasitic absorption losses. Finally, the best initial result demonstrating 9.9% efficiency on a plastic substrate textured by a nano imprinting replication process is presented.

EXPERIMENTAL DETAILS

We used the texture that develops naturally on zinc oxide when grown by low pressure chemical vapor deposition (LP-CVD ZnO:B) [6]. This texture consists of pyramidal shapes whose size is controlled by the film thickness. On our 2 μm thick films, the pyramids have base lengths of typically 200-300 nm. The V shaped valleys between the pyramids have been reported to reduce the open circuit voltage (Voc) and the fill factor (FF) because they lead to the nucleation and propagation of defective material [7]. We attempt to avoid this detrimental effect by using a plasma treatment that rounds out the valleys into U-shapes. On top of the ZnO substrates, a 300 nm thick silver layer was deposited by DC sputtering (Univex 450B, Leybold, deposited at room temperature). Half of the substrates were subjected to thermal annealing in ambient atmosphere at 150°C for 50 minutes. Total (TR) and diffuse (DR) reflectance of the bare substrates (ZnO + silver) were analyzed with a spectrophotometer equipped with an integrating sphere (Lambda 900, Perkin Elmer). To observe the morphology modification after annealing, scanning electron microscopy (SEM) was performed both from a standard top view (JSM-7500TFE, JEOL) and by using focused ion beam (FIB) milling for obtaining a cross-sectional profile for imaging (FEI Helios).

The remaining half of the substrates was used as the back reflector in single junction amorphous cells. For cell deposition, the back reflector was completed by adding an aluminum-doped ZnO barrier layer of around 80 nm by RF sputtering at room temperature (Univex 450B, Leybold, 2 wt % Al_2O_3 ceramic target). The cells were deposited in an n-i-p sequence with thick doped layers to avoid collection problems, the nominal thickness of the i-layer was 200 nm. The front contact was made of another LP-CVD ZnO:B layer. The cells were characterized by measuring their IV characteristics with a dual lamp solar simulator (Wacom WXS-220S-L2) under standard test conditions (STC, 25°C, AM 1.5 G spectrum, and 1000 W/m^2). Voc and FF were extracted from the IV curves, the short circuit current (Jsc) of the device was determined from the EQE after weighting it with the AM1.5 G spectrum. Correction of the EQE using the total cell reflection yields the internal quantum efficiency (IQE), i.e. the ratio of collected charge carriers per absorbed photon.

In a separate experiment, we applied the annealing process to produce a high efficiency device on a flexible substrate on polyethylene naphthalate (Goodfellow, 125 μm thick). The texture was made using a high fidelity process of replication using UV nano imprinting [8, 9]. The reproduced texture was a 2 μm thick LP-CVD ZnO plasma-treated slightly more than the texture used in the first experiments. The cell deposition was similar to that explained above except for the use of slightly thinner doped layers, which were used to improve Jsc.

Further results and details on the bare substrates analysis and cells can be found in [10].

RESULTS AND DISCUSSION

Analysis of bare substrates

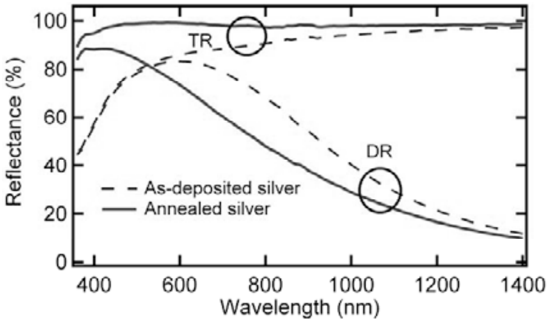

Figure 1: Bare substrate characterization: Total and diffuse reflectance of the silver samples.

Figure 1 compares the reflectance of the textured Ag films before and after annealing. In the as-deposited state, the total reflection is reduced by the strong absorption of short wavelengths. After annealing, the total reflectance is almost 100% over the entire wavelength range down to 360 nm, where the SPP resonance of the silver-air interface is expected in the presence of a rough surface. A reduction of the diffuse reflectance suggests reduced surface roughness after annealing.

Figure 2 shows SEM images of a top and a cross-sectional view. The SEM image of the annealed sample exhibits more rounded shapes than the as-deposited silver. The cross-sectional SEM images indicate that annealing results in a large reduction of the V shapes that can be observed in the as-deposited silver. It is interesting to note that the silver deposition itself brings out the pinched V shapes. The treated LP-CVD ZnO layer has few V shapes, but, as noted by the arrows on the right of the figure, a valley exhibiting a U shape develops into a V shape after silver deposition. This behavior suggests that a cell grown on top of the annealed silver, compared to a cell grown on the as-deposited silver, will not only benefit from improved optical properties but also from an improved Voc.

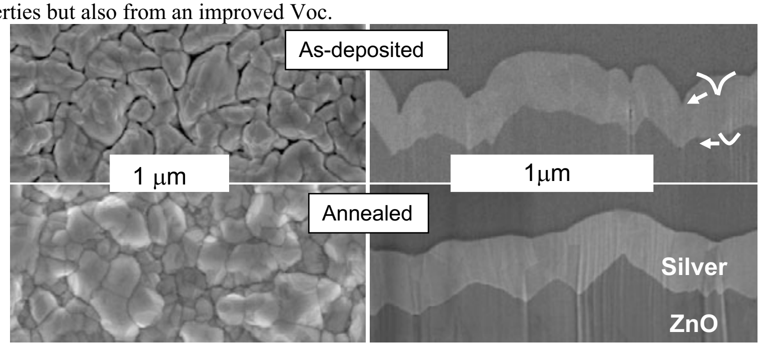

Figure 2. Bare substrate characterization: SEM images of the silver deposited on LP-CVD ZnO substrates; left) top view, right) cross sections made by FIB.

Cell analysis

Cells were co-deposited onto the same types of substrates as those describe above. Figure 3 shows that below 500 nm the cells behave identically because the incident light does not reach the back reflectors. Above 500 nm, more light reaches the rear part of the cell and is reflected by the textured silver back contact. The improved reflectance of the annealed silver film leads to more reflected light back into the cell for a second pass through the absorbing layer, resulting in higher EQE despite the lower total absorption of the cell. This conclusion is summarized in the IQE characteristics, which illustrate that the cell on the annealed reflector converts the absorbed light into collected carriers much more efficiently.

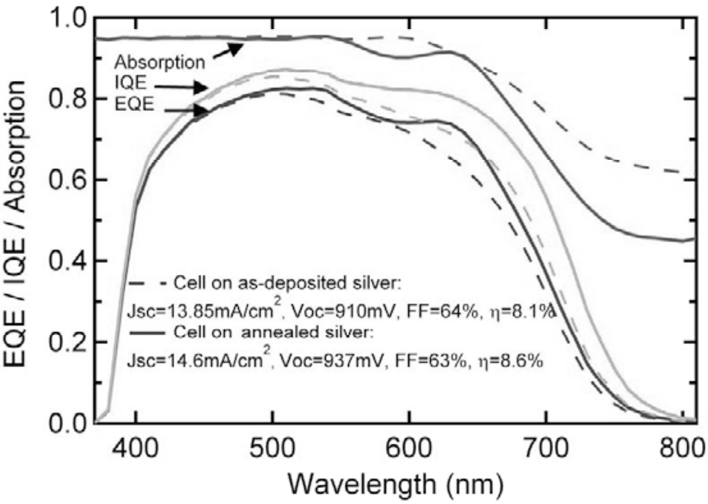

Figure 3: EQE, IQE and absorption measured on the cells with as-deposited silver and annealed silver back reflectors. The electrical parameters are also shown.

Interestingly, annealing decreases the surface roughness, as discussed above. Generally, a reduced roughness also yields cells with a higher Voc. The Voc of the cell on the annealed reflector is almost 30 mV higher and is well correlated with the reduction of the V shapes seen in the SEM images. However, a decreased substrate roughness also leads in general to lower light trapping. Based on the diffuse reflectance shown in Figure 1, we would expect less light scattering in the cell on the annealed reflector. The EQE in Figure 3 even shows interference effects in the cell grown on the annealed reflector, which is normally an indication of flat interfaces and poor light scattering. Nevertheless, the short circuit current density of the cell on the annealed reflector is almost 0.8 mA/cm^2 higher. Lower light scattering is therefore more than compensated by the better silver reflectance. In summary, a high efficiency improvement of 0.5% (from 8.1 to 8.6%) in absolute terms is observed, thanks to higher values of Jsc and Voc in the cell grown on annealed silver.

Best cell result on a flexible substrate using a replicated nano texture

Figure 4 shows the best cell result in terms of initial efficiency on a flexible substrate that has been textured with the replication of the LP-CVD ZnO surface texture via UV nano imprinting. An initial efficiency of 9.9% is obtained with a high current of 15.82 mA/cm^2. The silver annealing was performed as described above. This efficiency is better than that described above for several reasons. First, the cells shown in the previous section were fabricated with a robust base process, with relatively thick doped layers in order to avoid collection problems and to guarantee comparability across all cells of a series. Here, a compromise was achieved between a good Jsc for thin doped layers and good Voc and FF for thick doped layers. This improvement can be seen in the EQEs at short wavelengths; at 450 nm, the EQE of the cell on plastic is equal to 0.82, whereas at the same wavelength the EQE of the non-optimized cell on annealed silver presented above is equal to 0.76. Second, the deposition system cleaning history can explains the higher FF of this cell [11, 12].

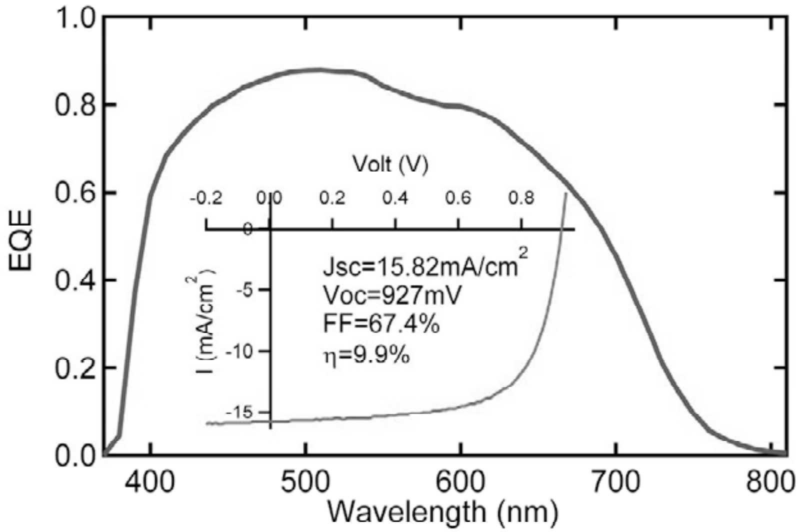

Figure 4: EQE and IV curve with corresponding electrical parameters for the best initial efficiency cell grown on a flexible substrate that was nano textured using UV nano imprinting.

CONCLUSIONS

Thermal annealing at moderate temperatures which allows the use of plastic substrates was performed on silver layers that serve as the back contact and reflector in thin film solar cells in n-i-p configuration. Several modifications to the silver film were observed; the reflectance increased substantially, the morphology changed towards a decreased substrate roughness and reduced V-shaped structures. The reflectance increase and the roughness decrease of the silver films are both beneficial for the cell device. The high reflectance reduces strongly the parasitic losses at the back reflector as can be observed in IQE curves. The decrease in roughness is beneficial in terms of Voc and also decreases the diffuse reflectance of the substrate, which in general leads to less light trapping. However, the high silver reflectance more than compensates for the light trapping losses, resulting in a higher Jsc value for the cell grown on the annealed silver reflector. An optimized cell on a flexible plastic substrate shows an initial efficiency of 9.9% and a current of 15.82 mA/cm^2.

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