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Ultra-thin LiF Layer As The Electron Collector For a-Si:H Based Photovoltaic Cell

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ABSTRACT

An ultra-thin LiF layer in conjunction with an Al layer is employed as the electron collector for the a-Si:H based single-junction thin film photovoltaic cell. The cell has the structure of boron doped μ-SiO$_x$ (hole collector) - intrinsic a-Si:H (photoactive layer) - LiF / Al (electron collector and back electrode). The substrate used is U type Asahi glass, which is also acting as the transparent front electrode. For the cell with the 1.5 nm thick LiF layer, annealed at 120°C, the open current voltage (V$_{OC}$) of 0.936 V, the short current density (J$_{SC}$) of 13.598 mA/cm^2, and the fill factor (FF) of 0.690 are achieved. The J$_{SC}$ and V$_{OC}$ values are comparable to the values measured for the a-Si:H based p-i-n reference cell, but the FF value is found to be lower, which is attributed to the losses due to recombination at the intrinsic a-Si:H / LiF / Al junction. The current versus voltage measurements are carried out under the standard test conditions. The J$_{SC}$ values are corrected according to the external quantum efficiency measurements of the cells in the AM1.5 spectrum region between 270 nm and 800 nm.

INTRODUCTION

Processing doped hydrogenated amorphous silicon (a-Si:H) layers involves handling expensive, toxic and flammable gases that contain the dopant atoms. In particular, phosphine (PH$_3$) used for n-doping of a-Si:H poses a significant health risk. It can form an explosive mixture in contact with air and oxidizing agents, even at relatively low temperatures of 40 – 50 ^{o}C [1].

The aim for this research is to replace n-doped a-Si:H by lithium fluoride (LiF). LiF is an insulator with narrow bands, a large work function and a wide band gap of 13.6 eV [2]. The wide band gap of LiF pushes the conduction band minimum beyond the vacuum level [3][4]. As a result, at the a-Si:H / LiF junction, the energy barrier experienced by the photogenerated holes in a-Si:H is expected to be larger compared to the energy barrier experienced by the photogenerated electrons. This means that an ultra-thin layer of LiF, which would allow direct tunneling of charge carriers [5], should be a good replacement for the n-doped a-Si:H layer [6]. Among the metals that are used as back reflecting electrodes for solar cells, LiF is found to work well with Al but not well with Ag [7][8].

The use of LiF / Al for collecting photogenerated electrons was first demonstrated in organic photovoltaic cells [9][10]. Subsequently, the concept was used for a-Si:H based thin film cells [11][12], and for crystalline silicon based cells [13]. So far, the efficiencies reported for these cells under the standard test conditions have been rather low. However, it is shown here that it is possible to achieve high efficiency for a-Si:H based thin film cells with LiF / Al rear layers. In this cell design, replacing the n-doped a-Si:H layer with the LiF layer eliminates the

health risks, and the laboratory health and safety requirements associated with the use of PH$_3$ gas during cell processing. In addition, the fact that LiF can be thermally evaporated makes its processing relatively simple for device construction.

EXPERIMENT

Photovoltaic Cell Design and Processing

The proposed a-Si:H based solar cell has a structure, in which a 300 nm thick intrinsic a-Si:H layer is sandwiched between a16 nm thick p-doped (boron doped) μ-SiO$_x$ layer and a combo layer of 1.5 nm thick LiF and 300 nm thick Al, where the LiF layer is located between the intrinsic a-Si:H layer and the Al layer. In this cell configuration, LiF layer replaces the n-doped a-Si:H layer of the conventional single-junction p-i-n configuration. Here, the a-Si:H based cell with the LiF layer is referred as the p-i-L cell.

For the p-i-L cell, the intrinsic a-Si:H layer is the photoactive layer responsible for the charge carrier generation under illumination. The μ-SiO$_x$ layer acts as both the window layer and the hole collection layer. The U type Asahi glass substrate functions as the transparent front electrode, where photogenerated holes accumulate. The photogenerated electrons tunnel through the ultra-thin LiF layer, and then they are collected at the rear Al electrode.

Boron doped μ-SiO$_x$ and intrinsic a-Si:H layers are deposited by a plasma-enhanced chemical vapor deposition (PECVD) cluster without breaking vacuum between these layers, onto a U type randomly texturized Asahi glass substrate, which is coated by a transparent layer of fluorine doped tin oxide (SnO$_2$:F). The surface of the intrinsic a-Si:H layer is exposed to air for about 30 minutes. The LiF layer is deposited by the thermal evaporation method and the Al layer is evaporated by the electron beam method; sequentially without breaking vacuum in the same physical vapor deposition (PVD) cluster.

The reference cells processed here have the standard superstrate p-i-n core structure, in which a 300 nm thick a-Si:H photoactive layer is sandwiched between a 16 nm thick p-type μ-SiO$_x$ hole collection layer and a 20 nm thick n-type a-Si:H electron collection layer. These silicon based layers are deposited in that order onto a U type Asahi glass substrate in the aforementioned PECVD cluster without breaking vacuum. The reference cells have the rear electrode structure of a 300 nm thick Ag layer, a 30 nm thick Cr layer, and a 400 nm thick Al layer; all deposited in that order in the aforementioned PVD cluster without breaking vacuum. The Ag layer is thermally evaporated. The Cr and Al layers are evaporated by the electron beam method. The surface of the n-doped a-Si:H layer is exposed to air for about 30 minutes before the Ag / Cr / Al rear electrode deposition.

After completing the deposition steps, the solar cells are annealed in a conventional oven in the air atmosphere.

Characterization

In order to determine the current density-voltage (JV) characteristics of the photovoltaic cells, a single flash lamp PASAN (class AAA) AM1.5 solar simulator system is used, where the flash spectrum matches to the AM1.5 spectrum with an irradiance intensity of 100 mW/cm^2. As well as generating the current voltage data, this system also measures the series resistance (R$_S$) and the shunt resistance (R$_{SHT}$) of the cells.

The fill factor and the open current voltage values are determined from the JV characteristics. However, the short current density values from the JV characteristics are often inflated. This is mainly due to the fact that photogenerated charge carriers are also collected from the absorber surrounding the active cell area that is defined by the reflective back electrode. In order to eliminate the uncertainty, therefore, the J_{SC} values are calculated from the external quantum efficiency (EQE) measurement data, which is independent of the active cell area and also of the light source.

In this work, the EQE measurements are carried out by an in-house built EQE system with a solar simulator matching to the AM1.5 spectrum between 270 nm and 800 nm.

Both JV and EQE measurements are taken at room temperature under ambient conditions.

DISCUSSION

The effects of annealing for the p-i-L cell are investigated by keeping the freshly deposited cells in a conventional oven at 120°C for one hour. According to table 1, post deposition annealing improves V_{OC}, FF, R_S, and R_{SHT}.

Table 1. The pre- and post-annealing J_{SC}, V_{OC}, FF, R_S, and R_{SHT} values for the p-i-L cell and the post-annealing J_{SC}, V_{OC}, FF, R_S, and R_{SHT} values for the p-i-n reference cell. The V_{OC}, FF, R_S, and R_{SHT} values are from the JV measurement data, and the J_{SC} values are from the EQE measurement data.

Anne. Temp. (°C)	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF	R_S (ohm.cm^2)	R_{SHT} (ohm.cm^2)
piL / ambient	12.430	928	0.541	15.233	894
piL / 120	13.598	936	0.690	9.848	1234
pin / 120	13.955	963	0.738	6.131	1550

The best performing p-i-L cell has FF of 0.690, V_{OC} of 0.936 V, and J_{SC} of 13.598 mA/cm^2. The J_{SC} and V_{OC} values are comparable to the values measured for the p-i-n reference cell, but the FF value is found to be noticeably lower for the p-i-L cell. This is main reason why the efficiency of the p-i-L at 8.78% is noticeably lower than that of the reference cell at 9.92%.

In order to determine the effects of replacing the n-doped a-Si:H layer with the LiF layer on the short current density, the external quantum efficiency measurements are carried out at 0 V (no bias) and at -1 V (reverse bias) for the p-i-L cell. Under the reverse bias, the EQE values increase over the entire visible spectrum, resulting in an overall increase of 0.28 mA/cm^2 in the short current density for the p-i-L cell.

CONCLUSIONS

As indicated by the high efficiency of the reference cell at 9.92%, the absorber film can be assumed to be of high quality. Therefore, the increase in the short current density under reverse bias for the p-i-L cell is very likely to be resulting from the insufficient collection of the photogenerated charge carriers from the intrinsic a-Si:H absorber. This could be resulting from the non-ideal junction of intrinsic a-Si:H / LiF / Al. Air exposure between the a-Si:H and LiF / Al deposition steps could also be causing contamination at the a-Si:H surface. This would reduce the junction quality, hence would increase the amount of photocarrier recombination at the a-Si:H / LiF / Al junction.

According to table 1, the short current density of the p-i-L cell is slightly less than that of the reference p-i-n cell. Since the LiF layer has a wide band gap and it is only 1.5 nm thick, the light absorption in this layer should be negligible compared to the absorption in the thicker n-doped a-Si:H layer with the much narrower band gap. Therefore, one reason for the reduced short current density of the p-i-L cell with respect to the p-i-n reference cell could be resulting from the lower reflectivity of the Al electrode for the longer wavelengths compared to the Ag electrode, as it is experimentally observed for a-Si:H based p-i-n cells that, at the photon wavelength of 600 nm, the reflectivity values for Al and for Ag are 0.70 and 0.87 respectively [14].

In solar cells, the series resistance is usually associated with voltage drops across the charge transport layer. This means that, the decrease in the series resistance for the annealed p-i-L cell would increase V_{OC} of the cell. This is indeed the case, as shown in table 1. Even though LiF is an insulator with a very wide band gap, the series resistance of the p-i-L cell remains relatively low. This is likely to be due to tunneling of the photogenerated electrons from the intrinsic a-Si:H absorber to the Al electrode via the ultra-thin LiF layer.

The shunt resistance is another type of parasitic resistance. R_{SHT} is associated with the leakage current, hence it influences the fill factor greatly. As shown in table 1, the increase in the shunt resistance due to the annealing step is reflected in the increased FF value of the p-i-L cell. However, as given in table 1, the fill factor of the p-i-L cell is noticeably lower than that of the p-i-n reference cell. This indicates that the leakage current could be still significant for the p-i-L cell. The relatively low R_{SHT} of the p-i-L cell can be attributed to local non-uniformities in the ultra-thin LiF layer, allowing Al to diffuse into the absorber. This would increase the amount of recombination at the a-Si:H / LiF / Al junction.

The main room for improvement for the p-i-L cell could come from depositing the cell without breaking the vacuum, preventing contamination due to the air exposure prior to LiF deposition. This should be the next topic of investigation.

The p-i-L photovoltaic cells processed in this work are not optimized. The power conversion efficiency of the best p-i-L cell is 1.14% less than that of the reference cell, primarily due to the inferior FF of the p-i-L cell. However, the respectable V_{OC} and J_{SC} values measured for the p-i-L cell indicate that the optimized ultra-thin LiF layer could be a good candidate to replace n-doped a-Si:H layer from the p-i-n cell structure.

The optimized p-i-L photovoltaic cell would reduce the use of silane and also eliminate the use of phosphine gas, therefore, making the thin film a-Si:H based photovoltaic cell manufacturing process safer and potentially cheaper.

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