Development Of Low Cost Germanium Photovoltaic Cells For Application In TPV Using Spin On Diffusants

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Abstract. At IMEC presently germanium photovoltaic cells are being developed for application in mechanically stacked solar cells. These stand-alone germanium cells can also be applied in thermophotovoltaic (TPV) systems. Simulations using the spectrum of an Er_2O_3 selective emitter heated by a butane burner have been performed to find the most optimal cell parameters. This results in a maximum simulated cell efficiency of 21 percent. In the applied cell process, the emitter is realized by using a spin-on diffusant and it is passivated using amorphous silicon, deposited by PECVD. Germanium photovoltaic cells have been realized with an AM1.5 efficiency of 6.7 percent, which is amongst the best germanium stand-alone solar cell efficiencies reported in literature.

INTRODUCTION

Mechanically stacked multi-junction solar cells are being developed at IMEC, for potential application in space. Germanium photovoltaic cells are studied as bottom cells in this mechanical stack, as well as stand-alone cells in hybrid lighting systems. These cells can also be applied in thermophotovoltaic (TPV) systems, since the general spectra used in these systems match the absorbance of germanium.

In order to realize an efficient and low cost TPV system, it is essential to use cheap substrates and low cost processing steps. Compared to other low band gap semiconductors, germanium is relatively cheap and thus is an excellent candidate for application in these systems.

Over the last decade, more and more groups have started research on germanium photovoltaic cells. Initially, most research has been focused on monolithically stacked multi-junction cells, where the junction in the germanium substrate is realized by diffusion of As from the GaAs layer grown by MOCVD [1, 2]. More recently single-junction cells are being developed by various research groups, efficiencies of 6 percent [3] under the AM1.5 spectrum and 13 percent [4] under concentrated light have been presented.

An important aspect in the realization of highly efficient single junction cells is surface passivation. In the past this turned out to be difficult; one of the reasons for this is that germanium oxide is hygroscopic (i.e. attracts water) and thereby degrades the electronic properties. A variety of materials have been examined for their surface

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passivation properties, like for example GaAs [4], SiN [3], SiO_2 [5] and amorphous silicon [6]. At this moment, not much data is available on the exact passivation properties of these materials. In future it will be important to use a material that can be deposited by a low cost method.

This paper describes the development of germanium photovoltaic cells done in our laboratory. In the next paragraph, simulation results are presented that indicate the potential of germanium solar cells illuminated by a selective emitter used in a TPV system. Subsequently the experiments done to realise germanium photovoltaic cells are described. To keep processing costs to a minimum, spin-on diffusants are used to realize the p-n junction. Finally, in the last paragraph the solar cell results are described.

SIMULATION

Simulations have been carried out, using the simulation program PC1D [7], in order to determine the optimal emitter depth, optimal substrate and emitter doping level and to study the influence of surface recombination using both a typical spectrum of an Er_2O_3 selective emitter and the AM1.5 solar spectrum.

To simulate the cell structure using a spectrum typical for a TPV system, various spectra can be chosen. In this case, the spectrum of an Er_2O_3 selective emitter heated by a butane burner has been used [8]. The spectral data, given in $W\cdot cm^{-2}\cdot nm^{-1}$, had to be adapted for use in PC1D, since the program expects a value in $W\cdot cm^{-2}$. Important to note is that PC1D scales the given spectrum according to the total power defined in the simulation file. The part of the spectrum that is not absorbed by germanium encloses a big part of the total power. For the simulation of the photovoltaic cell, it is assumed that this part can be completely reflected and recycled and in this way can be absorbed by the germanium cell. In reality, a recycling of 100 percent will not be possible, but this does not influence the behavior of the cell itself. The radiation power of the total spectrum is 9.9 $W\cdot cm^{-2}$ [8], assuming 100 percent reflection of wavelengths above 2030 nm results in a power of the adapted spectrum of 0.79 $W\cdot cm^{-2}$.

TABLE 1. Overview of PC1D simulation parameters.

	AM1.5	**Er_2O_3 spectrum**
Band gap (E_g)	0.664 eV	0.664 eV
Intrinsic concentration (n_i)	$2.33\cdot10^{13}$ cm^{-3}	$2.33\cdot10^{13}$ cm^{-3}
Electron mobility (μ_e)	3895 cm^2/Vs	3895 cm^2/Vs
Hole mobility (μ_h)	2505 cm^2/Vs	2505 cm^2/Vs
Bulk recombination (tau $_{bulk}$)	500 μs	500 μs
Back reflectance	30 %	30 %
Substrate thickness (t)	170 μm	400 μm
Substrate temperature	25 °C	50 °C
Illumination intensity	0.1 $W\cdot cm^{-2}$	0.79 $W\cdot cm^{-2}$

An overview of the simulation parameters is given in table 1. All results presented are obtained using a p-type substrate and a n-type emitter. Because of the weak absorption of the wavelengths close to the bandgap, a thicker substrate is required for optimal absorption when using the Er_2O_3 spectrum compared to the AM1.5 solar spectrum. To get a maximum efficiency the cell thickness should be around 400 μm.

The influence of the substrate and emitter doping concentration on the cell efficiency in a TPV system is given in Figure 1 and 2, respectively. As shown here, the optimum values for the substrate and emitter doping concentration are $1 \cdot 10^{15}$ and $5 \cdot 10^{17}$ cm^{-3}, respectively. When using the AM1.5 solar spectrum however, a clear optimum of the substrate doping level is found between $8 \cdot 10^{16}$ and $2 \cdot 10^{17}$ cm^{-3}. The shift in optimum substrate doping concentration is caused by the change in spectral distribution and cell thickness. In case of the spectrum emitted by Er_2O_3, most of the photons will be absorbed deep in the substrate and have to diffuse over a large distance to get to the depletion region. Since the minority carrier lifetime, and thus diffusion length, decreases with increasing doping level, a lower substrate doping level will be beneficial.

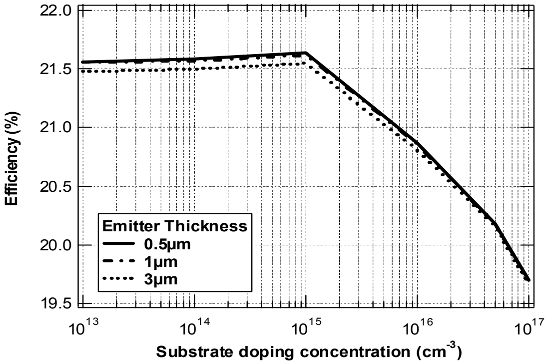

FIGURE 1. Influence of the substrate doping concentration of a germanium TPV cell simulated using an Er_2O_3 spectrum, assuming 100 percent reflection of wavelengths above 2030 nm; the emitter doping concentration is $5 \cdot 10^{17}$ cm^{-3}.

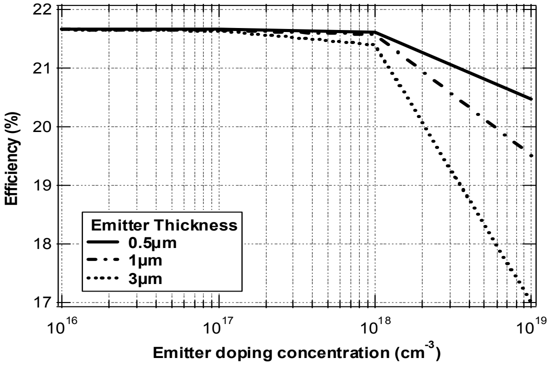

FIGURE 2. Influence of the emitter doping concentration of a germanium TPV cell simulated using an Er_2O_3 spectrum, assuming 100 percent reflection of wavelengths above 2030 nm, the substrate doping concentration is $1 \cdot 10^{15}$ cm^{-3}.

The influence of surface recombination is simulated using both the AM1.5g and the spectrum of the heated Er_2O_3 emitter, using similar cell parameters. Apart from the varied spectrum, a cell thickness of 170 and 400 µm has been used for the solar and TPV spectrum, respectively. Under the solar spectrum, the surface recombination should preferably be less than 200 cm/s, while under the TPV spectrum a higher surface recombination velocity is allowable, as shown in Figure 3. This is related to the lack of high energetic photons, the increased cell thickness and the increased intensity of the TPV spectrum.

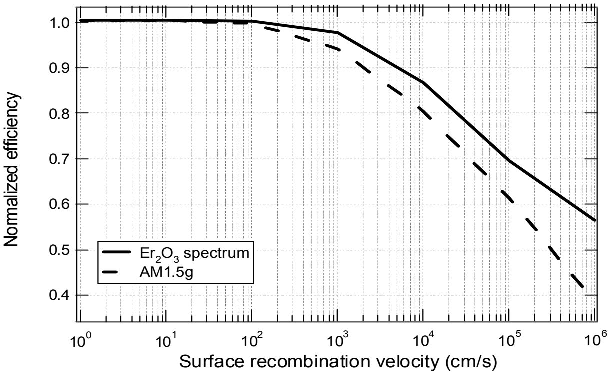

FIGURE 3. Influence of the surface recombination velocity on the efficiency of a germanium photovoltaic cell simulated using both the spectrum of the heated Er_2O_3 selective emitter and the AM1.5g solar spectrum. To compare the efficiency obtained in both cases, the efficiency is normalized.

Comparing the two optimal cell parameter sets, it is shown by simulation in PC1D that using a TPV spectrum asks for a lower doping level and an increased cell thickness compared to the optimal parameters for the AM1.5 solar spectrum. Furthermore the need for efficient surface passivation is less stringent. Another aspect that was not considered in the simulations is the resistance of the contacts. These should be optimized for the increased current density in case of the TPV spectrum. A maximum simulated cell efficiency of 21 percent is obtained.

EXPERIMENT

The cell process that has been developed in the research described in this paper basically consists of six steps. The method used to realise a sufficiently shallow emitter using spin-on dopant sources and the process to apply a passivation layer and subsequently realising a contact to the emitter are innovative steps [6]. A schematic illustration of the realised cell is given in figure 4.

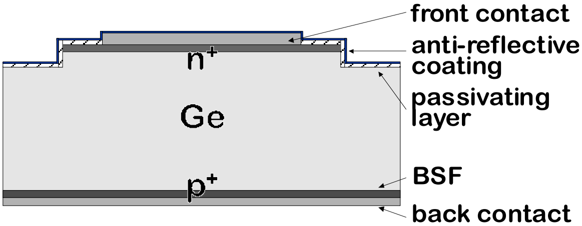

FIGURE 4. Schematic illustration of the realized germanium photovoltaic cell.

Cleaning the germanium substrate before and during the solar cell processing is done by a three step cleaning recipe using subsequently HCl/H_2O_2, NH_4OH/H_2O_2 and HF solutions. Since several of these steps are etching germanium slightly, the cleaning time is kept to a minimum.

The first main step of the cell process is the diffusion of the n^+ emitter in a lowly doped p-type germanium substrate. The emitter is created using a phosphorous containing spin-on dopant source, which is applied by spin coating. Several products with various dopant concentrations are available commercially. Here, a moderately doped spin-on dopant source is used. The diffusion time has to be kept short at relatively low temperatures to obtain a shallow emitter and avoid surface roughening. The diffusion time and temperature have been optimised to get a sufficiently shallow emitter.

The back contact and the Back Surface Field (BSF) are realised by evaporation of an aluminium layer and subsequent diffusion of the aluminium into the substrate to create a highly doped p^+ zone.

The various cells placed on one substrate are separated by MESA etching using a NH_4OH/H_2O_2 solution.

The fourth process step, the passivation of the front surface, is crucial for obtaining high cell efficiencies. For this a very thin layer of amorphous silicon is deposited by application of Plasma Enhanced Chemical Vapour Deposition (PECVD). The surface treatment applied before the actual deposition and deposition parameters like substrate temperature, plasma power and layer thickness are of major influence to the degree of passivation that will be obtained.

A silver (Ag) finger grid is used as the front contact. The silver is diffused through the isolating passivation layer to obtain the contact. This newly developed step is used, because uniform and selective wet etching of the amorphous silicon layer is extremely difficult due to the high reactivity of germanium. The diffusion time and temperature have been optimised in order to improve the cell's efficiency. In case of application in a TPV system this diffusion process should again be optimized because of the much higher current density that will be generated.

The cell process is finalized evaporating an anti-reflective coating, consisting of ZnS and MgF_2.

RESULTS

The emitter is realized by applying phosphorous-doped spin-on oxide using spin coating. Since the emitter should be only a few hundred nanometers thick, the diffusion time should be kept short and the temperature should be moderate. Furthermore, the thickness of the spin-on oxide influences the emitter profile [9]. As shown by SIMS analysis, presented in Figure 5, a spin speed of 4000 rpm and a diffusion temperature of 580 °C results in an emitter thickness of 215 nm, while at 3000 rpm a thickness of approximately 250 nm has been obtained.

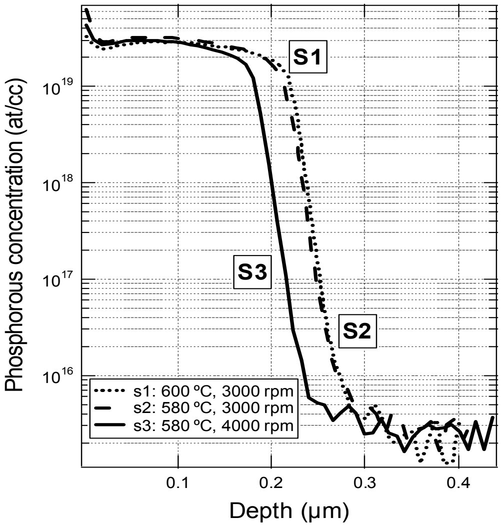

FIGURE 5. SIMS profiles of phosphorous diffused in lowly doped germanium, where the diffusion temperature and spin speed have been varied.

Passivation of the surface is obtained by using a thin layer of amorphous silicon deposited by *direct* PECVD. Especially important to get a good surface passivation is the preliminary treatment of the surface. Using an *in situ* hydrogen plasma, right before the actual deposition, improves the passivation properties by a factor of 2 or more. Using Photo-Conductance decay (PCD) measurements, effective minority carrier lifetimes up to 500 µs have been obtained on p-type germanium substrates with a bulk resistivity of 1 Ohm·cm.

The front contact is realized by diffusion of silver through the passivation layer. Since a layer of amorphous silicon is already deposited, the diffusion temperature should be kept below 250 °C to maintain its passivation properties. Furthermore the diffusion time should be optimized in order not to diffuse through the emitter. SIMS measurements are currently being performed to further study this process.

The best germanium solar cell realized so far resulted in an AM1.5 efficiency of 6.7 percent, which is amongst the best germanium stand-alone solar cell efficiencies reported in literature. The cells show a short circuit current (I_{sc}) of around 45 mA/cm^2 and an open circuit voltage (V_{oc}) of 245 mV. Figure 6 and 7 show the current-voltage and quantum efficiency curves, the latter indicating the extreme broad region of response of the realized cells, which is a proof of the excellent surface passivation that has been obtained.

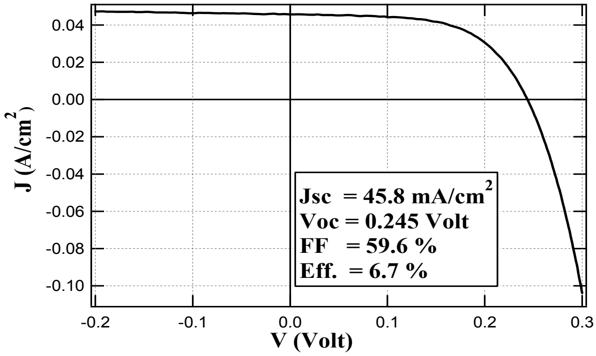

FIGURE 6. Current-Voltage characteristic of the realized germanium solar cell, measured using the AM1.5 spectrum.

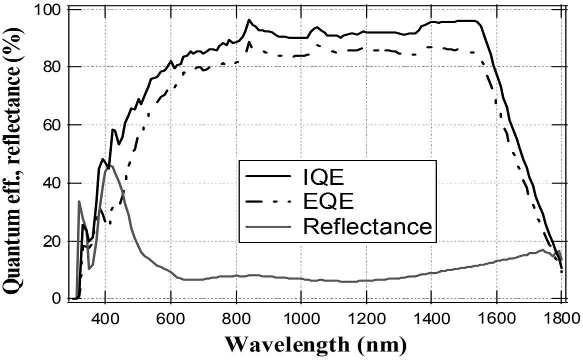

FIGURE 7. Internal, external quantum efficiency and reflectance curves of the realized germanium solar cell.

CONCLUSIONS

Germanium photovoltaic cells that are being developed for application in mechanically stacked highly efficient solar cells are also applicable in thermophotovoltaic systems. Simulations show that a lower substrate doping level and an increased cell thickness are beneficial for cells optimized for application in a TPV system compared to the cells designed for AM1.5 spectrum.

Up to now, an AM1.5 cell efficiency of 6.7 percent has been achieved, with a short circuit current density (J_{sc}) of 45.8 mA/cm^2 and an open circuit voltage (V_{oc}) of 245 mV. This cell has been realized using spin-on diffusants to create the p-n junction, which is a low cost and easy to use method. Diffusion temperature and spin-speed have been optimized to obtain a shallow emitter. Furthermore, PECVD amorphous silicon is used to passivate the germanium surface. Applying a hydrogen plasma before the amorphous silicon layer is deposited, seriously enhances its passivation properties. An effective lifetime of 500 μs has been measured using Photo-Conductance decay (PCD). The front contact is realized by diffusion of silver through the passivation layer. SIMS measurements are currently being performed to further study this process and eventually adapt it for a higher current density when used in a TPV system.

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