Development of Low-cost Thermophotovoltaic Cells Using Germanium Substrates

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Abstract. Stand-alone germanium solar cells, intended for application as bottom cell in mechanically stacked solar cells, have been realized applying an innovative process where the front contact is diffused through the a-Si passivation layer to establish the contact. The developed germanium solar cell process has resulted in world-class energy conversion efficiencies above 8 percent (AM1.5G). To optimize germanium cells for use in TPV applications, where an increased cell response at high wavelengths is desirable, an innovative back-side contacting mechanism has been developed. In order to increase the back surface reflection properties of the cell, laser fired contacts have been optimized and used. Using this contact, a germanium thermophotovoltaic cell with an AM1.5 energy conversion efficiency of 6.3 percent has been realized, showing an improved response at high wavelengths compared to the classical germanium solar cell. Cost estimations show that, by integrating this type of germanium photocells in a TPV system, an electricity cost of 1.9 €ct/kWh is achievable when assuming a system efficiency of 10 percent and a photocell cost of 6000 €/m^2.

INTRODUCTION

At IMEC currently germanium photovoltaic cells are being developed for application in thermophotovoltaic (TPV) and hybrid lighting systems [1]. Germanium cells are well suited for application in these systems, since the emitted spectra match the absorbance of germanium. In order to realize an efficient and low cost TPV system, it is essential to use low-cost substrates and processing steps. Compared to other low bandgap semiconductors, germanium is relatively inexpensive.

When a photovoltaic and a TPV system are compared, two basic differences are important with respect to cell development. First of all, in a TPV system the incident spectrum has a peak at a higher wavelength due to the relatively low temperature of the heat source compared to the temperature of the sun. Secondly, as a result of the small distance between the heat source and the TPV cells, a high current density will be generated. Where the high current density imposes more stringent requirements of the contacts, the high wavelengths of the incoming photons necessitates the application of light trapping to obtain high absorption.

This paper describes the recent development of germanium photovoltaic cells done in our laboratory. Improvements on the already developed germanium photovoltaic cells, such as an improved back surface reflection, will be presented. First an overview of the developed process is given and cell results will be presented.

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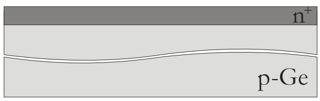
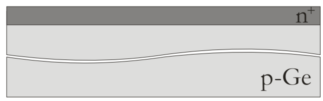
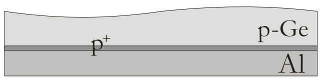
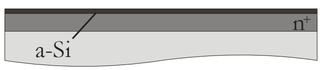
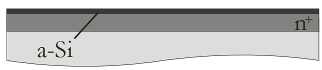
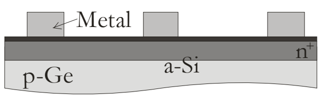
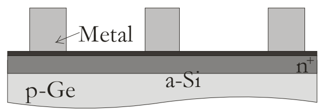
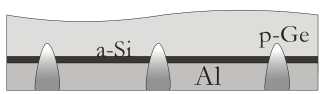
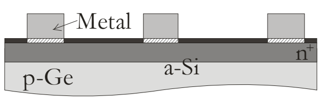
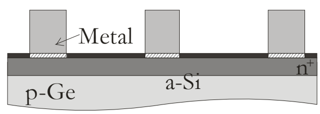
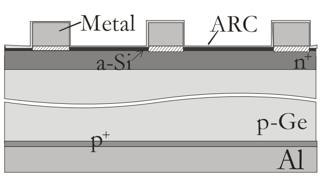
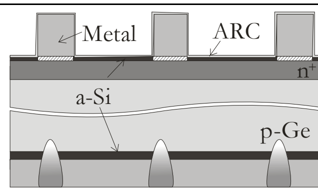
Finally, a comparison of cost estimations of TPV cells based on germanium and other semiconductors is presented.

CELL FABRICATION

In this research the development of a germanium TPV cell, based on a stand-alone germanium photovoltaic cell is described. The process that has been developed in the research described in this paper basically consists of seven steps. A schematic illustration of the processing of a classical germanium solar cell (designed for use under the AM1.5 spectrum) as well as the improved steps for the realization of a germanium TPV cell with increased reflection at the rear using laser fired contacts (LFC) is given in Table I.

TABLE I. Overview cell processing of a classical and LFC contacted germanium photovoltaic cell

#	Detail	Classic germanium solar cell	LFC contacted thermophotovoltaic cell
1	Emitter formation		
2	Backside processing		
3	Application of front surface passivation		
4	Deposition of front contact		
5	Laser fired contact		
6	Annealing of front contact		
7	Application of anti reflection coating		

The application of an a-Si passivation layer and subsequently realizing a contact to the emitter, and the realization of backside contacts by laser firing are innovative steps [2].

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.

Starting with a bare p-type, 145µm thick, 4-inch germanium substrate with a polished front side and a doping level of $1\cdot10^{17}$ cm^{-3}, first an n^+ emitter is realized by diffusion of phosphorous from a spin-on dopant which is applied by spin coating, see Table I, step 1. The diffusion profile is optimized by changing the phosphorous concentration in the spin-on dopant, the spin speed and the diffusion temperature and time [3].

As a next step, the backside of the photovoltaic cell is being processed (Table I, step 2). In order to obtain a low back surface recombination velocity in combination with a low contact resistivity, in the classical germanium process an aluminium (Al) layer is deposited which is subsequently annealed to realize an Al-Ge eutectic layer. Since aluminium is a p-type dopant in germanium, a p^+ layer is formed which serves like a back surface field (BSF). As a consequence of the eutectic layer, the back surface is roughened which leads to a lowered back surface reflection. Because effective light trapping is important in thermophotovoltaic cells, a highly reflective backside is one of the important aspects. Improved optical reflection can be realized by applying a single metal layer without an annealing. In this case, passivation of the backside can be achieved by the application of an amorphous silicon layer by Plasma Enhanced CVD (PECVD), which is also used for front-surface passivation and is transparent for the incident light in a thermophotovoltaic system.

The passivation of the front side is a crucial step, which will be used in both the classical and the LFC contacted cell (Table I, step 3). To obtain high quality surface passivation, the surface preparation method is of utmost importance. It is critical that all the germanium oxide present on the surface is effectively removed before the amorphous silicon layer is deposited. This germanium oxide layer is formed both by native growth in air and by application of the wet-chemical cleaning steps containing oxidising chemicals like H_2O_2. In addition to the surface pre-treatment, important parameters are the deposition temperature, plasma power and layer thickness. On lowly doped substrates ($2\cdot10^{14}$ cm^{-3}) a surface recombination velocity of 20 cm/s has been measured [4].

As a consequence of the use of amorphous silicon for germanium surface passivation, the processing possibilities with respect to front contact formation are restricted (Table I, step 4). Here, a double layer of Pd and Ag will be deposited on the amorphous silicon passivation layer. The formation of the font contact will be done in step 6 with an annealing and will be discussed in more detail in the subsequent paragraphs. In case of application in a TPV system the process for the realization of the front-contact should be optimized and the finger pattern should be re-designed because of the much higher current density that will be generated.

As a next step (Table I, step 5) contact at the backside will be realized by local heating with a laser. Using this technique the aluminium layer is locally heated and contact is being made. Subsequently an annealing is done, in order to realize the front-contact by diffusing the Pd through amorphous silicon passivation layer (Table I, step 6). More details will be given in the subsequent paragraphs.

The cell process is finalized (Table I, step 7) by evaporating an anti-reflective coating, consisting of ZnS and MgF_2.

EXPERIMENTAL RESULTS

Reflection Measurements

Measurements have been done, where the reflection as function of the wavelength has been measured from the front side of the sample, for germanium substrates having an anti-reflective coating and different backside contacts, as shown in Figure 1.

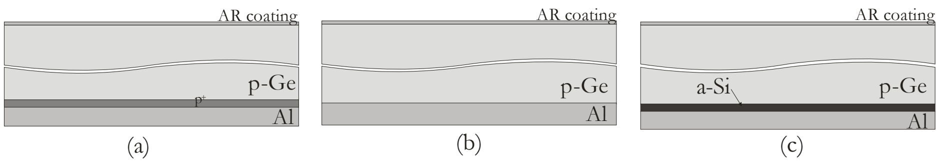


FIGURE 1: Overview substrates for different reflection measurements.

The results of these measurements are given in Figure 2 where one can see the low reflective properties of a diffused aluminium backside contact (see Figure 2 (a)). This can be explained by the fact that an Al-Ge eutectic layer is formed during the annealing which roughens the back surface, leading to a lower reflectance at the backside. Application of an aluminium layer without annealing (see Figure 2 (b)) leads to an increase of the (total) reflection at high wavelengths up to 50 percent. Since no BSF is formed in this situation, an alternative backside passivation technique needs to be applied.

As germanium surface passivation using PECVD amorphous silicon has proven to be effective, also the backside is passivated with amorphous silicon, see Figure 2 (c). Using an a-Si/Al backside contact, a reflection of 30 percent at 1800 nm is measured which is almost 20 percent absolute increase compared to an annealed aluminium contact. It is expected that a higher reflectance can be realized by optimizing the thickness of the amorphous silicon layer. Since amorphous silicon is insulating, contact can be made using so-called laser fired contacts (LFC), which is discussed in more detail in the next section.

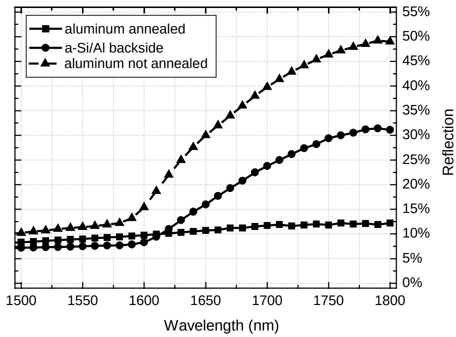


FIGURE 2: Measurement of the reflection of germanium substrates with different metals at the back.

Laser fired contacts

An innovative method to realize local contacts on a germanium substrate through an insulating layer like amorphous silicon is by laser firing. In Table I, cell 5 the process for realizing laser fired contacts (LFC) [5] is shown. After passivating the backside using PECVD amorphous silicon an aluminium contact layer is deposited by evaporation. Subsequently the metal will be heated locally by applying a laser pulse. For this application a green (532 nm) YAG laser is used. Local heating results in the formation of an eutectic compound between aluminium and germanium, forming the contact.

Aluminium is most suited because a local p^+ layer is obtained near the contact that serves as a back surface field. Aluminium also shows highly reflective properties as shown in Figure 2.

In first experiments, the laser power applied on the substrate has been optimized by changing the laser current through the laser diode, the propagation speed of the laser head and the focus of the beam. By changing the focus, the applied power can be spread over a larger area which results in a larger contact area with a lower power.

In Figure 3 a SEM image of a cross-section of the contacted area is shown. A clear change of structure at the laser-heated area is visible. Transfer Length Method (TLM) measurements has been applied to verify that an Ohmic contact has been formed with a specific contact resistance of $7.6 \cdot 10^{-4}\ \Omega \cdot cm^{-2}$.

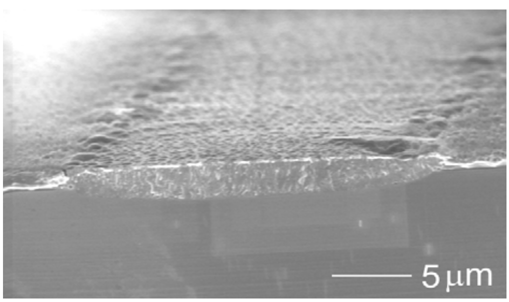


FIGURE 3: SEM image of laser fired contact between germanium and aluminium.

Front contact formation

Since for a classical germanium solar cell with a diffused back contact and for a germanium TPV cell the front side is fully covered with amorphous silicon, an innovative method for contact formation has been investigated. Here, the metal is diffused through the amorphous silicon to make to contact through the emitter [6]. Important are the specific properties of the diffusing metal, diffusion temperature, diffusion time and furthermore the thickness of the amorphous silicon layer. The best front contact is obtained by application of a double metal layer consisting of palladium (Pd) and silver (Ag). Pd is used to obtain fast diffusion through the amorphous silicon layer [7] and at the same time get limited diffusion in germanium. The additional layer of Ag is needed to lower the series resistance.

Depending on the thickness of the amorphous silicon layer, for a given annealing temperature, a clear evolution of the solar cell fill factor is observed as a function of annealing time. This behaviour is illustrated in Figure 4, where the IV-curve of a germanium solar cell is given as function of annealing time. Annealing for an even longer period of time results in a slight decrease in series resistance, however simultaneously a decrease in shunt resistance leading to gradual shunting of the solar cell is observed.

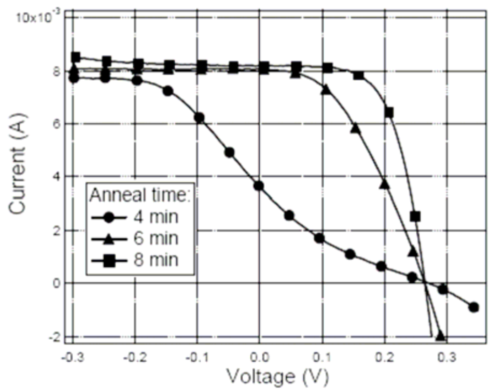


FIGURE 4: Illustration of the evolution of the IV-curve of a germanium solar cell, as a function of annealing time of the front side contact consisting of Pd/Ag.

SOLAR CELL RESULTS

Solar cells with a diffused backside contact

The developed germanium solar cell process has resulted in world-class energy conversion efficiencies above 8 percent (AM1.5, C=1 sun). Today, our best realized 1×1 cm^2 germanium solar cell has an AM1.5G efficiency of 8.1 percent, as shown in Table II. Furthermore a 0.5×0.5 cm^2 cell has been realized with a record efficiency of 8.4 percent, with a J_{sc} of 50 mA/cm^2, a V_{oc} of 258 mV and a FF of 65 percent. The applied anti-reflective coating consists of a double layer of ZnS and MgF_2, optimized for the AM1.5G spectrum.

Table II: Overview of realized germanium solar cell parameters (AM1.5G, C=1 sun), as measured at IMEC.

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	Efficiency (%)
Best 1×1cm²	47.8	255	66.4	8.1
Best 0.5×0.5 cm²	50.2	257.7	64.8	8.4

Solar Cells with Laser Fired Contacts

Laser fired contact germanium thermophotovoltaic cells have been realized using a rear contact pattern consisting of lines. These lines have a width of 20 μm and a spacing of 500 μm which leads to a total metallization fraction of 0.05 which was calculated to be the optimum [8].

In Table III, the results of 2 fabricated 1x1 cm^2 solar cells, A and B, are given, for different front contact annealing times [3] and with an additional double layer anti-reflective coating consisting of ZnS and MgF_2.

For cell B, the IV characteristics measured at the three different stages is given in Figure 5. These measurements show the formation of the contact at the front by annealing the solar cell. After an annealing of 5 minutes, in cell A no contact was observed but in cell B contact has been realized but still with a low fill-factor due to a high series resistance, as shown in Figure 6. After a additional annealing of 15 minutes, contact has been formed in both cells and a large improvement of the fill-factor was measured, but local shunting of the emitter is expected since the fill factor is non-optimal due to a lowered shunt resistance. The total diffusion time of 20 minutes was slightly too long for this specific solar cell.

Table III: Overview Cell Results of germanium TPV cells, measured using the AM1.5 spectrum, 1 sun.

no	total diffusion time	ARC	V_{oc} (V)	I_{sc} ($mA \cdot cm^{-2}$)	FF (%)	η (%)
A	5 min	No	251.1	14.1	18.6	0.7
	20 min	No	234	35.2	47.1	3.9
	20 min	Yes	244	44.8	53.6	5.6
B	5 min	No	246.6	34	44.3	3.7
	20 min	No	243	35.1	60.3	5.1
	20 min	Yes	243.1	44.5	58.5	6.3

After applying the anti-reflective coating for both cells an improvement of the current was observed without a significant decrease of the fill factor which proves the quality of this contact.

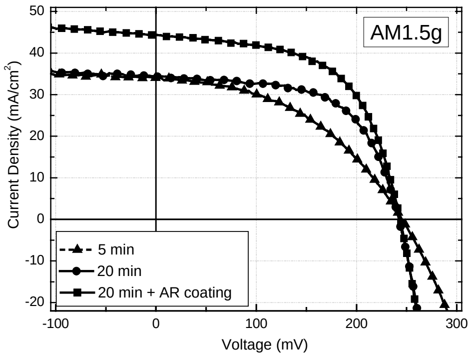
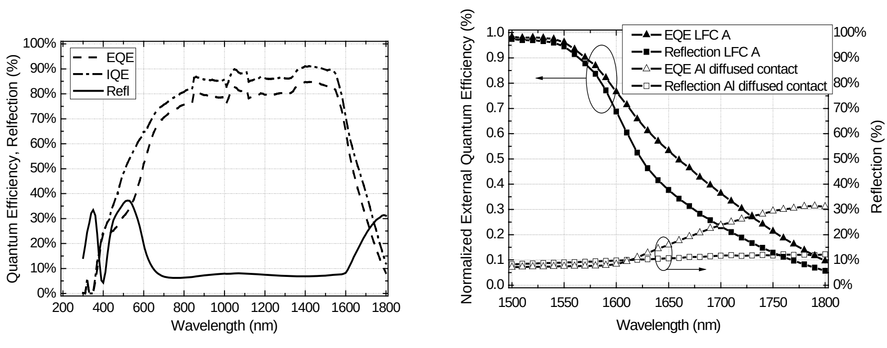


FIGURE 5: IV characteristics of the germanium solar cell B (AM1.5g).

Cell B resulted in an AM1.5 efficiency of 6.3 percent with a short circuit current density (J_{sc}) of 44.5 mA·cm^{-2}, an open circuit voltage (V_{oc}) of 243.1 mV and a fill-factor (FF) of 58.5 percent.

Figures 6 (a) and 6 (b) show the quantum efficiency curves of cell B demonstrating the improved response of this cell in the high wavelength regions compared to the classical germanium cell with a diffused aluminium rear contact.

The most important motivation for using laser fired contacts in germanium TPV cells is improved light trapping properties caused by enhanced reflection at the rear. This is clearly illustrated in Figure 6. In Figure 6 (b) the reflectance and normalized EQE which has been measured on the 2 different types of germanium solar cells has been compared. Each cell has the same emitter and front contact grid, but one cell has a diffused aluminium rear contact and the other a LFC contact. One can observe a better EQE for high wavelengths in combination with a higher reflectance.



(a) (b)

FIGURE 6: (a) Spectral response of a germanium TFV cell using LFC back contact. **(b)** normalised external quantum efficiency (EQE) and reflection of a laser fired and a classical contacted germanium solar cell.

COST ESTIMATIONS

In order to assess the economic potential of germanium (Ge) thermophotovoltaic cells, a cost estimation has been done, based on the estimates published previously by G. Palfinger et.al. [9, 10]. Here, for several different scenario's, the total cost in eurocents per kWh is calculated so the system returns its investment over the lifetime. All costs, including emitter, glass tube, photocells and cooling elements added with €100/W_{peak} for miscellaneous were included. The results of these estimations are given in Table IV.

Scenario Ge1 applies the cost as in Si2 (except for the cells) and a system efficiency of 5%; the cost of the germanium photocells is based on the current germanium substrate cost (10000 €/m^2) and a processing cost of 1000 €/m^2, which can be considered realistic given the large similarities of the applied process with standard Si solar cell processing. This yields an energy cost of 5.5 €ct/kWh. Scenario Ge2, improving the system efficiency to 10% (in line with the system efficiency predicted for another low bandgap photocell system [11]) and assuming a 50% reduction of the germanium substrate cost (which can be achieved by reducing the substrate thickness and surface finish requirements), results in an achievable energy cost of 1.9 €ct/kWh.

TABLE IV. TPV Cost Estimations. Data for scenarios Si1, Si2 and GaSb is taken from [11]. Ge1 applies the cost as in Si2 (except for the photocells for which a realistic price based on the actual cost of Ge substrates is put forward) and a system efficiency of 5%; Ge2 improves the system efficiency to 10% and assumes a 50% reduction of the substrate cost

Scenario	Si 1	Si 2	Ge 1	Ge 2	GaSb [11]
photocell area (m^2)	0.2	0.1	0.1	0.1	0.1
system efficiency (%)	1	1.5	5	10	12.3
peak thermal output power (kW)	20	20	20	20	12.2
peak elec. output power (kW)	0.2	0.3	1	2	1.5
average thermal input power (kW)	13	13	13	13	7.9
average elec. output power (kW)	0.13	0.2	0.65	1.3	1
photocells (€)	200	120	1100	600	
quartz tube (€)	190	59	59	59	
emitter (€)	62	62	62	62	
cell-cooling (€)	120	0	0	0	
€100/W_{peak} for miscellaneous	20	30	100	200	
total investment (€)	**590**	**270**	**1320**	**920**	**2900**
total investment/kW_{peak} elec (€)	3000	900	1320	480	1930
yearly elec production (1800h) (kWh)	230	350	1200	2400	1800
€ct/kWh (20y lifetime)	**13**	**3.8**	**5.5**	**1.9**	**8**

CONCLUSIONS

Cost-efficient thermophotovoltaic cells can be realized by using germanium substrates. In order to achieve high conversion efficiencies, the application of light trapping in germanium thermophotovoltaic cells is very important. A higher back surface reflection together with a good back surface passivation can be reached by using an aluminium layer, together with an amorphous silicon passivation. Electrical contact is formed through laser fired contacts.

An AM1.5 cell efficiency of 8.4 percent has been achieved using a classical diffused aluminium backside contact. First experiments on the realization of germanium photovoltaic cells using a laser fired back contact have yielded an AM1.5 cell efficiency of 6.3 percent, with an increased response at high wavelengths as compared to the classical cell.

Further research will be done to test the cell performance under a TPV spectrum emitted by a heat source. Mainly the performance of the front- and back contact under high light intensities is of main interest. Also a further optimization of the laser fired contacts will be done, where the realization of a dotted pattern is one of the objectives.

ACKNOWLEDGMENTS

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The cells were measured against a reference cell which is calibrated (traceable) to the World Radiometric Reference by the European Solar Test Installation (ESTI) of the European Commission Joint Research Centre, an ISO 17025 accredited calibration laboratory.

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