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Epitaxial growth and electrical characterization of germanium

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Ge homojunctions were deposited by means of Metal Organic Vapour Phase Epitaxy (MOVPE) on Ge substrates at 550 °C and 675 °C, using AsH_3 as n-type dopant. Ge_n/Ge_p, $GaAs_n/InGaP_n/Ge_n/Ge_p$ and $Ge_n/Ge_p/Ge_p$ structures were prepared and studied, where n and p identify the layer or substrate doping. Vertical mesa junctions were obtained on the above structures by using conventional photolithographic and evaporation techniques. The junctions were characterized by I-V measurements under dark and illumination conditions and by EBIC technique. It has been observed that the samples grown at lower temperature showed better rectifying I-V characteristics and light conversion efficiency while EBIC results may suggest that a high As diffusion is present in the samples grown at higher temperature.

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1 Introduction

Ge is a semiconductor widely used for infrared detection, photovoltaic (PV) applications and high mobility electronic devices [1]. There is also interest in using it instead of GaSb for thermophotovoltaic (TPV) applications, because of its cheaper price, larger substrate size and wider availability: although Ge has an indirect band gap with respect to GaSb, there are several efforts to develop a technology to utilize Ge cells in TPV apparatus to reduce the overall cost of the TPV system [2,3].

Since Ge epitaxy is not very common, Ge junctions both for PV and TPV devices are usually realized by diffusing a suitable dopant on the substrate surface, forming a thin emitter layer. The most common process is to deposit a GaAs or InGaP layer [4]. The drawback of this method is that it is impossible to obtain sharp junctions and to control the emitter thickness and doping profile. Better results in terms of cell open circuit voltage (V_{OC}), short circuit current (I_{SC}) and fill factor (FF) could be obtained by depositing an epitaxial Ge layer with well defined thickness and doping concentration. Developing an epitaxial Ge deposition process would also allow to realize novel high efficiency cell structures, such as the ones described in [5].

The aim of our epitaxial Ge growth study is to develop a process to fabricate Ge cells for thermophotovoltaic application [6]. Usually Ge layers are deposited by ultra high vacuum evaporation techniques, but the development of an MOVPE deposition technique for Ge layers is important because it would permit to couple Ge and well-assessed III-V epitaxy such as GaAs, AlGaAs and InGaP. Moreover, MOVPE is the most used commercial technique for the mass-production of optoelectronic and high efficiency solar cell devices.

2 Experimental

Ge layers were deposited by means of Metal Organic Vapor Phase Epitaxy (MOVPE) system using iso butyl germane (iBuGe) as metal organic precursor and H_2 as carrier gas. All the growths were performed at 60 mbar, and two series of samples were grown at 550 °C and 675 °C. Before the growth the Ge substrates were thermally annealed at 650 °C for 5 min to remove the surface oxide. The first series of samples consists in epitaxial n-type Ge layers (Ge_n/Ge_p, the Ge_p being the substrate), about 400 nm thick and grown at 550 °C onto

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p-type substrates. On some of the above n/p junctions we added a 400 nm thick InGaP window layer and a 400 nm thick GaAs layer grown at 600 °C, in order to enhance the conversion efficiency of the $GaAs_n/InGaP_n/Ge_n/Ge_p$ structure. In this case the standard AsH_3, PH_3 (10% diluted in H_2), tri methyl gallium and tri methyl indium precursors were used. III/V and In/Ga ratio during GaAs and InGaP growths were 180 and 1.2 respectively.

The second series consists in two kinds of structures grown at 675 °C: i) a n/p junction (Ge_n/Ge_p) obtained by using a p-type substrate as the base and about 400 nm n-type Ge layer as emitter and ii) a fully epitaxial n/p Ge junction about 2.4 μm thick, on a p-type substrate ($Ge_n/Ge_p/Ge_p$). In this case the emitter thickness (Ge_n) was nominally 400 nm thick. The dopings of the n and p-type substrates were about $2x10^{17}$ cm^{-3} and $2x10^{16}$ cm^{-3} respectively. We achieved n-type doping by means of AsH_3, with different procedures depending on the growth temperature.

For the growths at low temperature the Ge substrate was initially flown with 250 sccm AsH_3 for 3 minutes. Then Ge was grown by injecting iBuGe for 10 min. The metal-organic flow was interrupted and AsH_3 was immediately re-injected in the chamber for another 3 min. After this step, AsH_3 was removed and the iBuGe was reintroduced in the reactor without any delay. The high gas velocity (0.5 m/s) ensures a fast gas switching between the reagents. Three of these cycles were used. For the growth at high temperatures iBuGe and 50 sccm AsH_3 were injected at the same time into the reactor for the entire growth process.

Ohmic contacts were obtained by evaporation, followed by a thermal annealing at 250 °C for 60 s, of Au on the backside of the p-type substrate and by evaporation of Au-Ge dots, 400 μm in diameter, onto the n-type epilayer. 500 μm mesa structures, concentric to the Au-Ge dots, were then prepared by chemical wet etching in a solution of H_2O_2:H_2O. Light conversion efficiency of the structures was measured using an AM1.5 solar simulator, rated 0.7 suns, and considering as the illuminated region the mesa area not covered by the Au-Ge dot. The structures were also tested under illumination of a Xe lamp by varying its power.

The $Ge_n/Ge_p/Ge_p$ samples were characterized by means of Electron Beam Induced Current (EBIC) in a Cambridge 360 Scanning Electron Microscope (SEM) operated at 20 keV with beam currents in the range 1-30 pA. EBIC measurements were performed in cross sectional view by using vertical mesa junctions as the ones described above.

3 Results and discussion

The use of AsH_3 has a strong effect on the Ge growth [7-9]. In our growth processes we found that even a small addition of some sccm of AsH_3 in the gas phase along with iBuGe is able to reduce the growth rate up to 10 times. For this reason, in order to n-type dope the Ge layers with AsH_3 while achieving a reasonable growth rate, we used the procedure involving the alternate switching between AsH_3 and iBuGe in the gas phase, as described in the experimental section.

Ge n-type doping at low temperature has evidenced the presence of an AsH_3 memory effect in the reactor. When we deposited the homoepitaxial Ge in a clean environment, after removing the residuals of the previous growth from the quartz liner surrounding the graphite susceptor, intrinsically p-type doped samples with carrier concentration in the range 10^{18} - 10^{19} cm^{-3} range were obtained. With the use of AsH_3 the Ge conductivity shifts to n-type. If a second run is performed without the use of AsH_3 at the same temperature of 550 °C the sample is observed to be n-type doped even if no AsH_3 was present in the growth environment, suggesting that some AsH_3 remains adsorbed in the growth chamber along with Ge during the growth process.

In order to switch back to the p-type conductivity the quartz liner had to be cleaned from the growth residuals and a thermal annealing of the reactor performed. We tried to overcome this problem by raising the growth temperature to 675 °C and by growing another series of samples. The nominally undoped samples were still p-type and n-type samples were obtained again with the use of AsH_3. In this case no memory effect was observed and, after the AsH_3 run, we were able to re-obtain p-type doped layers without quartz cleaning.

This behaviour could be explained by the tendency of AsH_3 to react with the Ge deposits on quartz chamber walls during the growths at lower temperatures. We may suppose that at 675 °C all the AsH_3 is decomposed to species that are either not adsorbed on the quartz walls or are less prone to remain in the reactor, to be released in subsequent growth processes or to act as dopants for the Ge layer. At 550 °C incomplete cracking may occur and some AsH_3 adducts may be adsorbed on the quartz walls along with Ge and be released during the following processes. These adducts should not be present at 675 °C. The AsH_3 memory effect is present also if GaAs growths are performed in the same reactor before or after Ge deposition.

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In, Ga and P from InGaP deposition may have the same behaviour but we did not study their behaviour systematically. For this reason, after the growth of the GaAs/InGaP/Ge/Ge structure, we cleaned the reactor chamber in order to be sure that no unwanted elements were present in the reactor.

This memory effect may pose some limits to the processes that could be realized in an MOVPE deposition chamber. With a low temperature Ge growth process (550 °C) it is difficult to control the p-type doping and reactor cleaning, either with wet chemicals or with a thermal annealing, may be needed after each n-type doping run to revert to intrinsically p-type doped layer. However, we easily obtained Ge n/p junctions using a p-type Ge substrate as a base and an n-type Ge doped with AsH_3 as emitter. In this case the addition of AsH_3 is higher than the contaminant As present in the reactor because of the memory effect, and repeatable doping results could be obtained even at 550 °C.

Since the memory effect is avoided at high temperatures, we compared n/p junctions grown at 550 °C and at 675 °C. Figure 1 reports the I-V characteristics of samples grown at 550 and 675 °C, respectively. It has been observed that the samples prepared at higher temperature show lower rectification ratios and poorer light conversion efficiency in comparison with those obtained at 550 °C. The addition of GaAs and InGaP contact layers increases by almost an order of magnitude the rectification factor.

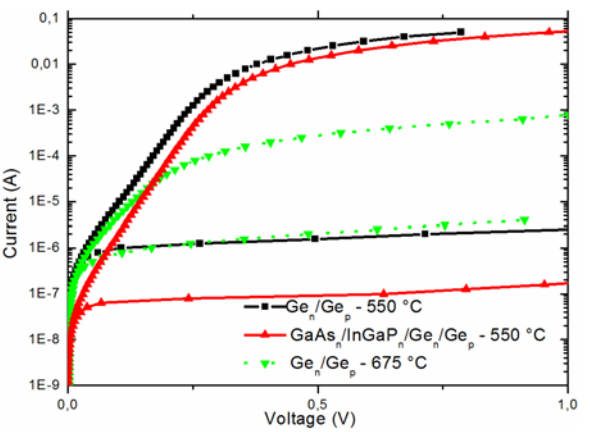


Fig. 1 I-V characteristics of the structures grown at different temperatures. (Online color at www.crt-journal.org)

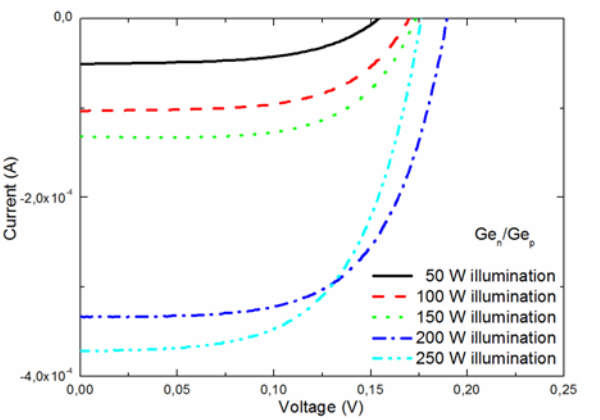


Fig. 2 I-V curves of Ge junctions grown at 550 °C obtained under different illumination by a Xe lamp. (Online color at www.crt-journal.org)

Table 1 characteristics of the Ge n/p junction grown at 550 °C under different illumination powers. (*measured by a Si photodiode)

Lamp Power (W)	I_{SC} (A)	V_{OC} (V)	I at max. power (A)	V at max. power (V)	Max. power out (W)	FF	Incident power density* (W/cm^2)
50	-5.03 x 10^{-5}	0.1538	-3.97 x 10^{-5}	0.10879	-4.32 x 10^{-6}	0.55789	0.0125
100	-1.03 x 10^{-4}	0.16981	-8.53 x 10^{-5}	0.12276	-1.05 x 10^{-5}	0.59988	0.0404
150	-1.32 x 10^{-4}	0.17282	-1.12 x 10^{-4}	0.12675	-1.42 x 10^{-5}	0.62356	0.0646
200	-3.34 x 10^{-4}	0.18882	-2.82 x 10^{-4}	0.13877	-3.91 x 10^{-5}	0.62152	0.115
250	-3.72 x 10^{-4}	0.1758	-3.04 x 10^{-4}	0.12775	-3.88 x 10^{-5}	0.59416	0.154

Figure 2 reports the I-V curve of the Ge/Ge sample grown at 550 °C under different illumination conditions using a Xe lamp, while the data extracted from the curves are shown in table 1. The measurements suggest that with higher power density device performance decreases, probably due to the increase of temperature of the devices during the measurement. This is a critical issue to use this device as a TPV converter, since high energy density are expected in this kind of application. Another set of measurements with the device coupled to a radiant heater apparatus, to be used as a TPV prototype, is planned in the near future.

We also measured the properties of the Ge_n/Ge_p grown at 550 °C and of the $GaAs_n/InGaP_n/Ge_n/Ge_p$ layers under an AM1.5 solar simulator, rated 0.7 suns. The I-V curves under illumination of the two structures are shown in figure 3, while the cell data are reported in table 2. The addition of the InGaP window layer and the GaAs contact layer increases the conversion efficiency by a factor of about 2: the addition of a top InGaP window layer acts to reduce the surface recombination velocity at the Ge surface, thus increasing the open circuit voltage [11], while the highly doped GaAs contact layer is added to reduce the cell series resistance and to improve the quality of the top ohmic contact. However, by comparing our data with the record efficiency

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results obtained from Ge cells designed for TPV applications, reported in [10], we note that our Ge_n/Ge_p efficiency results are worse by a factor of about 2, but we should also consider that our cells contacts and anti-reflection coating are still not optimised for best performances.

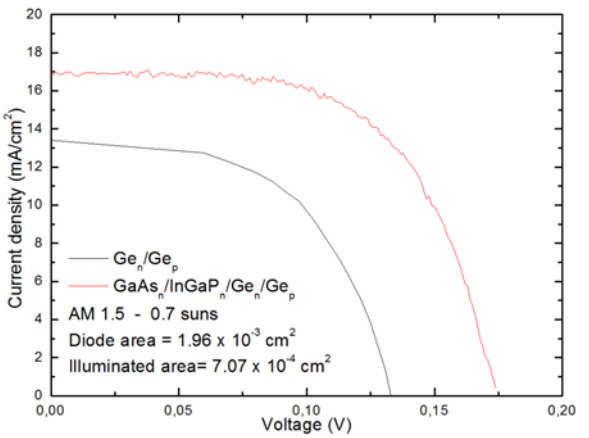


Fig. 3 I-V characteristics of the junctions grown at 550 °C under AM 1.5 illumination, 0.7 suns. Current density is obtained by considering the area of the 500 μm diameter mesa structure. Illuminated area is considered as the outer 100 μm ring without metallization. (Online color at www.crt-journal.org)

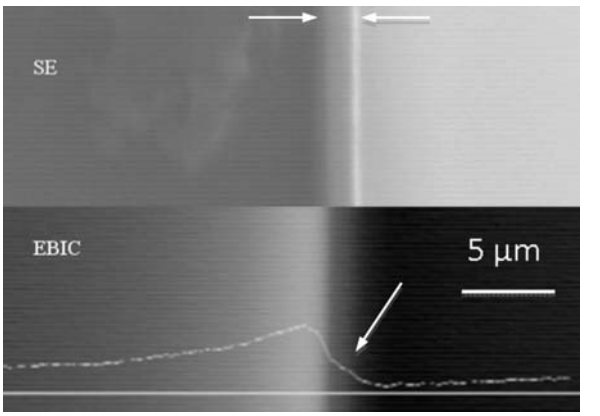


Fig. 4 Top: Secondary Electron (SE) cross section image of the Ge/Ge epitaxial junction. Ge substrate is on the left side, while the 2 horizontal arrows mark the epitaxial film as observed by SEM, including the contact layer. Bottom: EBIC image and EBIC current profile of the same zone imaged with SE. The arrow marks the second weak peak observed in the EBIC signal.

Table 2 Properties of the junctions grown at 550°C under AM 1.5 illumination, 0.7 suns.

Structure	I_{SC} (A)	V_{OC} (V)	Fill factor	Efficiency (%)
Ge_n/Ge_p	26.3 x 10^{-6}	0.133	55	3.9
$GaAs_n/InGaP_n/Ge_n/Ge_p$	33.4 x 10^{-6}	0.178	61	7.9

One of the reason for poor performances of junctions grown at 675 °C could be the enhanced As diffusion at high temperature. In order to get a better understanding about this behaviour we performed detailed EBIC measurements of a fully epitaxial n/p junction. The sample was grown on a p-type substrate (doping about $2x10^{16}$ cm^{-3}) with a first p-type epitaxial layer, nominally about 2 μm thick, and an n-type AsH_3 doped Ge layer, about 400 nm thick. Figure 4 shows the cross section SEM (top) and EBIC (bottom) images and the EBIC current profile across the junction, which shows the presence of a second very weak peak (indicated by the arrow) inside the epitaxial region: this could suggest the presence of a second junction there and that the structure consists of two diodes in series.

The space charge region seems located near the interface with the substrate and not, as expected, between the top n-type and the p-type epitaxial layer. A hypothesis to explain this behaviour could be the high diffusion of the n-type dopant across the epitaxial p-type region, up to the less doped p-type substrate. As is known to have a very high diffusivity with respect to the other p-type dopants. Following this idea, near the low doped p-type substrate an n/p region may be formed, which behaves like a second diode in series with the epitaxial n/p region. This must be verified by performing SIMS measurements and dopant element profiles in the future. In order to corroborate this hypothesis, we note that at the growth temperature of 675 °C the diffusion of As into p-type Ge is very fast [12], so that the achievement of a sharp junction seems to be very difficult: theoretical calculations [13] and SIMS analysis [14] showed that As could diffuse up to several microns in Ge. It was also proposed that As diffusion in Ge takes places mainly through vacancies [15], and if a high density of vacancy due to our epitaxial growth process is created during a high temperature deposition process this could also enhance As diffusion. The As diffusion at high temperature could lead to a broader n/p interface and could also explain the worse I-V curve shown in figure 1 and the unsatisfactory behaviour under AM 1.5 illumination of the sample grown at 675 °C.

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4 Conclusions

Ge epitaxial samples were grown by MOVPE at 550 °C and 675 °C. AsH_3 was used to dope the samples but different procedures were optimised depending on temperature to overcome the high reduction in growth rate observed at 550 °C. It has been shown that the low temperature samples exhibit I-V characteristics better than the ones grown at high temperature. The addition of a GaAs contact layer and an InGaP surface passivation layer enhanced the light conversion efficiency of the sample grown at 550 °C, as measured under AM 1.5, 0.7 suns simulator. Efficiencies up to 8.5 % were measured in $GaAs_n/InGaP_n/Ge_n/Ge_p$ devices. EBIC profiles could suggest a high As diffusion into a fully epitaxial n/p junction, with the As from the top n-type layer diffused through the p-type epitaxial layer down to the p-type substrate.

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