n and p-doped Germanium grown by MOVPE for solar cell applications

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Abstract

Growth of n and p doped Germanium on GaAs substrate and homo-epitaxy of Germanium was performed by Metalorganic Vapour Phase Epitaxy (MOVPE) using the new iso-butyl germane (IBuGe) source furnished by Rohm and Haas. The iso-butyl germane is a liquid metal-organic source with a cracking temperature of 350°C similar to that of Germane and with the advantage of being less toxic. There is no evidence in literature of p-doped Germanium obtained by MOVPE and this new approach will permit to realise for the first time a totally epitaxially grown InGaP/InGaAs/Ge/Ge Quadruple Junction. The control of doping, the influence of the different growth parameters on the morphology and the electrical characteristics of p and n-doped Germanium were studied by the mean of AFM (Atomic Force Microscopy) analyses, Hall Effect and ECV (Etching Capacitance-Voltage) measurements. As well, the absence of Germanium memory effect in the chamber was demonstrated. The I(V) characteristic of a Germanium diode totally grown by MOVPE were measured showing promising results in term of rectification ratios.

Introduction

The growth of Ge/GaAs or (In)GaAs based structures represents a strategic challenge for the realization of solar cells. The energy gap superposition between Germanium (0.66eV), GaAs (1.42 eV) and InGaP (1.88eV), can cover a large range of the solar spectrum leading to a very efficient absorption. Moreover the Ge/GaAs heterostructure is almost lattice matched and Ge has almost the same thermal expansion coefficient of GaAs. Thus, the Ge/GaAs heterostructure (or Ga(In)As/Ge) appeared to be the best candidate together with InGaP to form a multijunction solar cell [1]. However, by now, the third junction of an InGaP/InGaAs/Ge structure was realized by atom diffusion into Germanium substrate, obtaining not abrupt doping profiles [2]. As a consequence a reduced open circuit Voltage and short circuit currents can be expected with an epitaxial PN Ge junction.
In this study we obtained n and p doped Germanium grown on Ge and on GaAs substrate by Metal-Organic Vapour Phase Epitaxy (MOVPE) using the new iso-butyl germane (IBuGe) source furnished by Rohm and Haas [3]. So far there were no proofs in literature about p doping of Germanium directly by MOVPE, probably due to the high n background doping connected to the low band gap of Germanium. The possibility of realizing p-n Germanium junctions totally grown by MOVPE can introduce an important improvement in the performances of the devices. The doping during MOVPE growth permits to work in a single step process, achieving well defined junctions. This new approach will lead to realise InGaP/InGaAs/Ge/Ge QJ solar cells where the Germanium junction can be totally epitaxially grown with increased efficiencies.
We realized p-n junction diodes of Germanium both growing an epitaxial n (p) layer on a p (n) Ge substrate and growing a totally epitaxial p-n structure.
The nominally undoped Germanium was affected by a high background n-doping, around $6X10^{18}$ cm^{-3} and a saturation of free carriers concentration at high AsH_3 fluxes was evidenced. On the other hand at high growth temperature, the Arsine pressure did not influence the growth rate as observed in low temperature conditions in the case of Germane [4]. At high temperature the As monolayer, that turned out to passivate the surface, has been mostly desorbed. The p-doping was fairly well controlled by introducing TMGa during growth, showing a linear dependence increasing the TMGa flow between 10^{19} cm^{-3} and more than 10^{21} cm^{-3}. The TMGa and Arsine supplies produced very nice surfaces, with a low roughness of around 0.3 nm in a 20X20 μm size (Atomic Force Microscopy Image). From preliminary studies it was evidenced that p-n diodes totally grown by MOVPE showed very interesting features and rectification ratios higher than in the case of epitaxial layers forming PN structures with the substrate, with the possibility to modulate the doping concentration of the junction.

Experimental

The samples were grown in a low pressure MOVPE system VEECO D180, using a vertical chamber with a pressure of 70 Torr and Hydrogen as carrier gas with a total transport flow of 55000 sccm/min. For the

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Germanium deposition the recent Iso-Butyl Germanium (IbuGe) source from Rohm and Haas was at disposal. N and p-doped Germanium were grown respectively injecting Arsine (AsH_3) and TrimethylGallium (TMGa) during Ge layer deposition.
The IbuGe flow was fixed at 100 sccm, with the bath temperature fixed at 5°C and the bubbler pressure at 600 Torr (correspondent IbuGe partial pressure around $1.54X10^{-2}$ mBar), while the growth temperature was varied from 550 to 710°C. The vapour pressure of TMGa was changed in order to increase the range of doping (with a correspondent partial pressure between $1.07X10^{-6}$ and $1.57X10^{-4}$ mBar). Before the layer growth, we supplied Arsine during the substrate annealing at 650°C to Arsenic removal from the reactor walls. We have performed hetero-epitaxial growths on p-doped Germanium (001) 6°off ($2.7X10^{18}$ cm^{-3} doped with Ga) and N-doped Germanium ($1X10^{18} cm^{-3}$ doped with As) and on semi insulating GaAs (001).
The free carrier concentrations and the mobilities were studied by Hall measurements at room temperature (295 K) with Van der Pauw method. The doping profiles were measured by ECV (Etching Capacitance-Voltage), using a KOH 0.1M solution for Germanium etching. The morphology was investigated by Atomic Force Microscopy (AFM) in tapping mode.
The metallic contacts to measure the I-V characteristic were AuGeNi for the n-doped side and MnAu for the p-doped side and an annealing (350°C, 2 minutes) at hydrogenated Argon atmosphere was applied after the metallic depositions.

Results

With the aim to find the best growth conditions we have grown p-doped Germanium layers on Germanium 6°off and GaAs (001) substrates varying the growth temperature in a range between 550°C and 710°C, with a TMGa flux of 0.0135 sccm. We found that the growth rate increased with the temperature, because the deposition was still in kinetic regime conditions. From the Arrhenius plot (Fig.1) between growth rate and the reciprocal of the temperature we found an activation energy around 20.6 kcal/mol.
The epitaxial growth of Germanium at 670°C, showed a very good surface morphology both on Germanium and on GaAs, with a RMS roughness of 0.78 nm (in a 20X20 micron size) in the case of deposition on Germanium substrate.
Considering the convenient growth rate, we decided to work at 670°C to study the n and p doping. The nominally undoped Germanium was affected by a high background n-doping around $6.7X10^{18}$ cm^{-3} measured by Hall Effect. The n doping was increased to $2X10^{19} cm^{-3}$ supplying an AsH_3 flow of 10 sccm but the doping did not change much for 50 sccm, with a carrier density of $4X10^{19}$ cm^{-3} , evidencing a saturation, due to solid solubility limit (Fig.2).

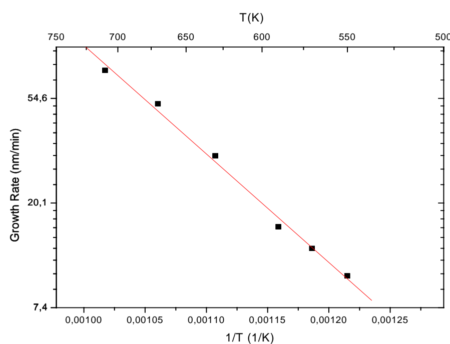

Fig.1 : *Arrhenius plot of Growth Rate versus 1/T for p-doped Germanium grown by MOVPE*

Therefore we obtained a carrier density range between $6X10^{18} cm^{-3}$ and $3X10^{19} cm^{-3}$. Additionally, we proved that in this temperature conditions Arsine did not affect too much the growth rate. This is in contrast with the characteristic that we observed in the case of lower temperature growth (550°C) where the growth rate decreased of about 5 times already at low Arsine Flows (Fig.3). That effect was already shown in several works and explained by the saturation of Germanium dangling bonds by Arsenic, thus responsible of a blocking effect [4].

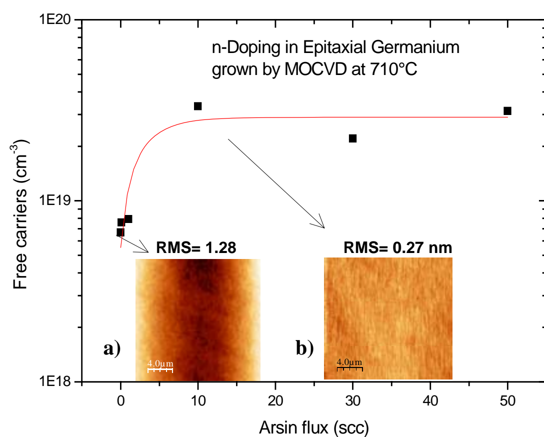

Fig.2 : *n doped Germanium with Arsine, between 0 and 50 sccm; Red line: Exponential fit curve; Inset: AFM images at 20X20 μm for Ge without Arsine (a) and with Arsine at 10 sccm (b)*

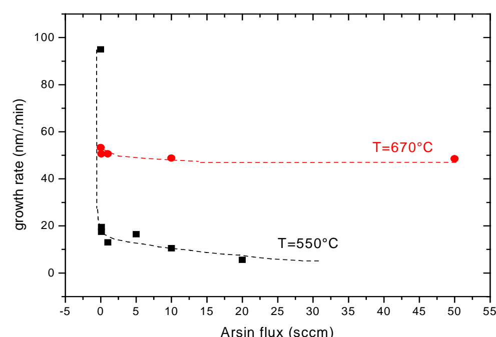

Fig.3: *Growth rate of Germanium doped with AsH_3 at 550°C (black squares) and at 670°C (red circles)*

Instead, in our case, at a growth temperature of 670°C, the deposition rate decreased only slightly and it ranged from 53 nm/min in absence of Arsine to around 46 nm/min supplying 10 sccm of Arsine. In this latter conditions, the morphology resulted even better than in the case of intrinsic Germanium evidencing a possible role of Arsine in flattening the surface, still at higher temperature, like already observed in lower temperature conditions [5]. In fact, the RMS roughness of the Germanium layer grown in presence of 10 sccm of Arsine was 0.27 nm in a 20X20 micron size (Fig.2, inset b) while the RMS roughness of an undoped Germanium was 1.28 nm.

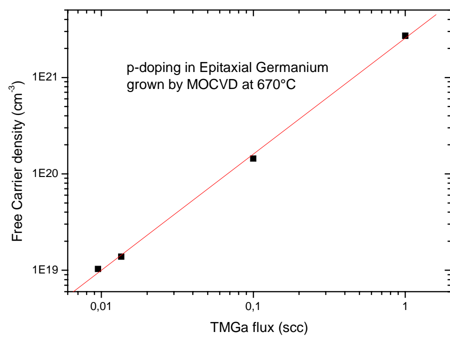

Fig.4: *p-doped Germanium with TMGa, between 0.0095 and 1 sccm*

On the other hand the p-doping was fairly controlled by introducing TMGa during growth with flows between 0.0095 sccm and 1 sccm at the same conditions previously described. We observed a linear dependence in the range between $1X10^{19}$ and $3X10^{21}cm^{-3}$ increasing the TMGa flows (Fig.4).
As in the case of Arsine, TMGa did not influence too much the growth rate. But this time, the layers with a TMGa flow of 1sccm presented pits on the surface, probably due to the formation of Gallium clusters that prevented further layer growth in localized zones.
The diffusion of As, Ga and Ge in a GaAs/Ge or Ge/GaAs during growth is known to be very strong and it must be possibly attenuated cause it could deteriorate the solar cell performances, changing the electrical characteristic of the different layers.
We dedicated a special attention on Germanium diffusion, cause Germanium acts like a donor for GaAs and it would tend to compensate the p doping or to increase the n doping in GaAs layers. In particular, we studied the possible presence of Ge memory effect for further GaAs growths. With this purpose a 2 μm thick GaAs layer was grown after the use of Germanium in the MOVPE chamber and compared to a 2 μm thick GaAs layer grown before the use of Germanium. They both presented a n carrier concentration around $1X10^{17}cm^{-3}$, measured by Hall effect, and very similar ECV doping profiles (not shown here). Therefore we demonstrated the absence of a Germanium memory effect in our reactor being the doping level of the same order of the n-type residual doping in our GaAs layers.
Using the growth conditions previously described, different types of Germanium diodes were realized and their I(V) characteristics were measured. A p-doped Ge epitaxial layer were grown on a n-doped Ge substrate. Furthermore PN diodes totally epitaxial were grown on a n-doped Ge substrate. In all the cases presented here the p-doped Germanium sides were doped with TMGa at 0.013 sccm with a carrier concentration around $2X10^{19}cm^{-3}$, while the n-doped Germanium sides were either undoped, therefore with an intrinsic n carrier density around $6.7X10^{18}cm^{-3}$, or doped with 10 sccm of Arsine with a doping level of $2X10^{19}cm^{-3}$ measured by Hall effect. Both the p and the n sides were around 1 μm thick.

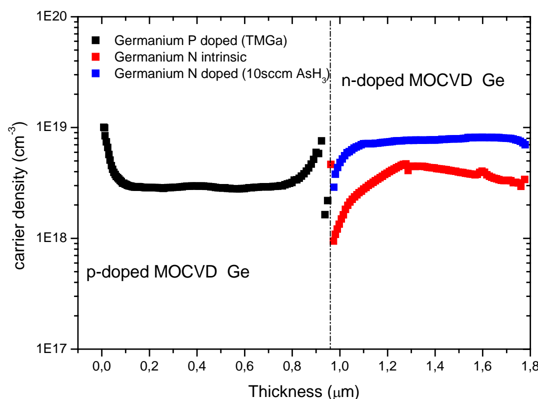

Fig.5: *ECV of a Ge-PN junction totally grown by MOVPE on for 2 different n doped layers*

As shown in Fig.5, the doping profile, measured with ECV, was quite constant for the p-side, a part from the interfaces, sensible to measures effects. On the other hand for the intrinsic doping layer (red curve in Fig.5), in the n side a decrease of the doping profile is evidenced at the p-side interface and along the profile. Instead, in the case of Germanium doped with Arsine (blue curve in Fig.5), the profile is more homogeneous and there is

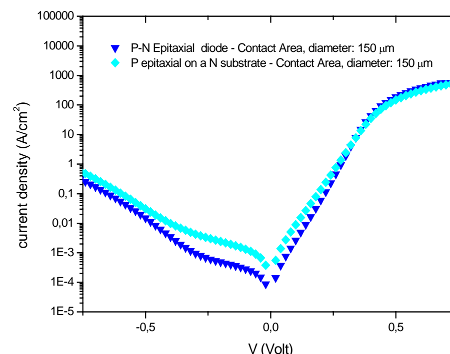

Fig.6: *I(V) characteristic of a Ge-diode totally grown by MOVPE (dark blue) and of a P MOVPE on N substrate diode (cyan)*

not a decreasing of the carrier density along the layer, probable because the n-doping is governed by the Arsine supplied.
Also if the technology was still in a phase of assessment, the pn diodes entirely grown by MOVPE showed very interesting I(V) behaviours, with rectification ratios higher than in the case of p layers grown on n-bulk substrates (Fig.6). In the case displayed here, for a contact area with a diameter of 150 μm, the rectification ratio for the totally MOVPE grown diode was around 670 at 0.24 V and 4510 at 0.5V, while it was around 205 at 0.24 V and 1480 at 0.5V for the p-doped Germanium grown by MOVPE on a n-doped substrate. Higher rectification ratios were caused by the more heavely doped p and n sides of the junctions and the consequent enhancement of the built-in voltage that tends to decrease the inverse current.
By the way, further studies are in progress to improve the performance of these devices, optimising the growth conditions and improving the I(V) contact quality.

Conclusions

We were able to realize Germanium p-doped by MOVPE with IbuGe and TMGa, obtaining a linear dependence between TMGa and p-type carrier density. Furthermore we performed the n-doping with Arsine up to a saturation level of $4X10^{19}cm^{-3}$. We evidenced the role of Arsine in flattening the surface and in controlling the doping profile. In unintentionally doped Germanium we found an intrinsic n-doping of around $6X10^{18}cm^{-3}$, probably connected to the IbuGe source. We realized PN Ge diodes totally grown by MOVPE with different conditions, observing good I(V) characteristics in all the cases.

Acknowledgements

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