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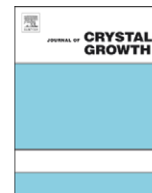

MOVPE growth of homoepitaxial germanium

M. Bosi [a,*], G. Attolini [a], C. Ferrari [a], C. Frigeri [a], J.C. Rimada Herrera [a,1], E. Gombia [a], C. Pelosi [a], R.W. Peng [b]

[a] CNR-IMEM Institute, Parco Area delle Scienze 37/A, 43010 Fontanini, Parma, Italy
[b] National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, PRC

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ABSTRACT

n-Type Ge epitaxial layers were deposited on p-type Ge substrates by means of metal-organic vapour phase epitaxy (MOVPE) at temperatures ranging from 500 to 600 °C using isobutylgermane (iBuGe) as metal-organic precursor and hydrogen as carrier gas.

The samples were grown at different iBuGe partial pressure conditions and were characterised by means of atomic force microscopy (AFM), high-resolution X-ray diffraction (HR-XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The layers grown with iBuGe partial pressure of 3.3×10^{-6} bar at 550 °C show a good crystallographic structure, flat surface and a good interface with the substrate, while for lower partial pressures a series of pits was evidenced on the layer. The pit density was found to be dependent on the growth rate. n-Ge/p-Ge diodes, obtained with standard photolitographic techniques, show rectification ratios higher than 10^5 and ideality factors in the 1.008–1.010 range.

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1. Introduction

With its bandgap of about 0.66 eV Ge is a widely used material in infrared detection, photovoltaic and thermophotovoltaic (TPV) conversion. However, the epitaxial growth of Ge is hindered by the tendency of Ge surface to roughen very easily, because of a order–disorder transition from $p(2\times8)$ to (1×1) surface reconstruction. This transition is temperature controlled and is a common problem for ultra high vacuum (UHV) deposition of Ge on Ge substrate using germane (GeH_4) as source [1]. Ge surface roughening has been studied by several groups and different growth methods have been proposed in order to overcome this difficulty [2–6]; however, the commonly used growth technique for Ge deposition is still either UHV or molecular beam epitaxy with pressure in the order of 10^{-10} Torr.

High efficiency triple junction (TJ) solar cells based on lattice mismatched InGaP/InGaAs/Ge have nowadays surpassed a conversion efficiency of 40% [7]. In this kind of structures the Ge junction is used to convert the part of the solar spectrum between 0.66 and 1.4 eV [8]. Ge cells are also employed in TPV devices instead of GaSb and several groups are trying to develop new methods to utilise Ge cells to reduce the cost of the TPV system [9,10].

The current technology used to obtain Ge p/n cells is dopant diffusion, starting from an n-type or p-type substrate [11–13]. The cell emitter is fabricated by flowing an appropriate precursor (arsine or phosphine for n-type doping, trimethyl gallium or dimethyl zinc for p-type doping) on the substrate surface at high temperature or by deposition of a GaAs layer and subsequent diffusion of Ga and As at high temperature. The drawback of the diffusion procedure is that broad dopant profiles instead of sharp junctions are obtained. Moreover, the experimental conditions must be precisely controlled in order to get a perfect reproducibility and a controlled doping profile.

Better photovoltaic conversion performances in terms of open circuit voltage (V_{OC}) could in principle be achieved with Ge cells by means of homoepitaxy of Ge on the Ge substrate, since the epitaxial process can easily control both the layer thickness and the dopant profile. For these reasons, the set up of a Ge epitaxial growth procedure using metal-organic vapour phase epitaxy (MOVPE) is desirable, since practically all the commercial compound semiconductor devices are mass produced with this technique.

Last, Ge-based electronic devices are recently gaining a new interest since Si device scaling down is rapidly approaching its limit. Due to its higher carrier injection velocity and mobility with respect to Si, Ge has been proposed as a possible candidate for the next generation of high transport channel devices [14].

* Corresponding author. Tel.: +39 0521 269288; fax: +39 0521 269206.
E-mail address: bosi@imem.cnr.it (M. Bosi).

[1] Permanent address: Laboratorio de Celdas Solares, Instituto de Ciencia y Tecnologia de los Materiales (IMRE), Universidad de La Habana, Colina Universitaria, 10400 La Habana, Cuba.

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In order to grow Ge layers by MOVPE, in addition to the use of GeH_4, a toxic and expensive hydride gas, several metal-organic compounds with Ge atoms, like trimethyl GeH_4 or monomethyl GeH_4 are available, but these compounds have high cracking temperatures. Isobutylgermane (iBuGe) is a novel metal-organic precursor which has a high vapour pressure at room temperature, decomposition onset of about 350 °C, low background impurity level, and is considerably less toxic than GeH_4. Therefore it could be a suitable candidate for the realisation of Ge epitaxial junctions in an MOVPE apparatus using the conventional temperature range for the deposition of III–V compounds [15–17].

In our previous work, we tried to overcome the roughness problem evidenced at higher iBuGe partial pressure by using arsine as surfactant either before the MOVPE growth itself or by adopting a procedure involving the use of several cycles of iBuGe and AsH_3 [18]. The work presented in this paper was aimed at growing Ge epitaxial layers without AsH_3, using lower iBuGe partial pressures and finding a balance between a good crystal structure and an appreciable growth rate.

2. Experimental procedure

Ge epilayers were deposited by means of a home made horizontal MOVPE equipment, using 2000 sccm H_2 as carrier gas. The graphite susceptor was heated by infrared lamps and the growths were performed between 500 and 600 °C at low pressure (60 mbar). The growths were carried out on three different substrates in the same growth run: two p-type-doped Ge substrates with different crystallographic orientations, one exactly (0 0 1) oriented (doping level of about $10^{16}\,cm^{-3}$) and another (0 0 1) miscut 6° off towards [1 1 0] (doping level of about $10^{18}\,cm^{-3}$), and an n-type doped (0 0 1) GaAs substrate misoriented 2° off towards [1 1 0]. GaAs substrates were used to selectively etch the Ge layer in order to perform thickness measurements with an alpha-step profiler. Native oxide was removed from the Ge substrate prior to the growth with an HCl wet chemical etching and by performing a thermal annealing of the substrate at 650 °C for 5 min before the film growth.

The standard process to realise Ge layers involved the use of iBuGe only, with the Ge layer directly deposited on the substrate at different temperatures and iBuGe partial pressures in the 10^{-7}–10^{-5} bar range after the substrate thermal cleaning step. As it will be discussed in the following sections, a good epilayer was obtained only by limiting the iBuGe partial pressure to about 4×10^{-6} bar.

The layers were characterised by atomic force microscopy (AFM) using a Digital Instruments Nanoscope IIIa in contact mode; numerical analysis in order to estimate surface roughness were performed using Nanoscope 6.12 software. High-resolution X-ray diffraction (HR-XRD) was obtained on a Philips X'Pert Pro diffractometer using the CuKα_1 line (1.54056 Å) and a four reflection Ge monochromator with an angular resolution of 12 arcsec. Scanning electron microscopy (SEM) images were acquired using a field emission scanning electron microscope (LEO 1530VP) while Raman spectra were obtained with a Labram Jobin–Yvon apparatus equipped with a He–Ne laser and a spectral resolution of about $2\,cm^{-1}$.

For transmission electron microscopy (TEM) observations both planar and cross-sectional specimens were prepared by bombardment with an argon ion beam under a vacuum of $\sim10^{-6}$ Torr after mechanical thinning down to 30 μm. TEM experiments were performed at 200 keV, mostly in the bright field mode under two beam diffraction conditions.

Vertical mesa n-Ge/p-Ge junctions were prepared on the above structures by using conventional photolithographic techniques. Ohmic contacts were obtained by evaporation of Au on the backside of the p-type substrate followed by a thermal annealing at 250 °C for 60 s and by evaporation of Au dots, 400 μm in diameter. The 500 μm mesa structures, concentric to Au dots, were then prepared by chemical wet etching in a solution of H_2O_2:H_2O. The current–voltage (I–V) characteristics of the fabricated diodes were measured by a Keithley 236 source-measure unit.

3. Results and discussion

Samples thickness was routinely measured on GaAs substrates; the value obtained with this method is in good agreement with the observations performed on TEM (within an error of less than 10%), meaning that the growth rate on GaAs and Ge is very similar. Fig. 1 reports the growth rate achieved for nominally undoped Ge layers grown between 500 and 600 °C at a constant iBuGe partial pressure of 3.3×10^{-6} bar. In this interval the growth rate is almost constant between 500 and 550 °C, while a decrease is observed at higher temperature. The reason for this drop could be ascribed to a variety of factors: for example at higher temperature, given the same precursor partial pressure, decomposition could be enhanced at the reactor inlet and part of the species could be deposited on the quartz liner or on the susceptor before the substrate itself, thus depleting the gas phase; this is reasonable due to the low cracking temperature of iBuGe. Moreover, above a certain critical temperature, the balance between adsorption and desorption of Ge could change and this could cause a decrease in the growth rate. We could not find useful informations about this fact related to Ge epitaxy on Ge in low pressure MOVPE, so that further studies should be directed in understanding the precise cause of this behaviour.

A detailed study was performed on samples grown at 550 °C: experiments performed at this temperature and in dependence of the iBuGe partial pressure showed a linear dependence between the growth rate and the iBuGe flow.

The layers deposited with iBuGe partial pressure less than 4×10^{-6} bar were all mirror-like with good crystallographic properties. By increasing the iBuGe partial pressure above this threshold, the surface morphology degraded abruptly and became milky and optically rough, regardless of the growth temperature. AFM analysis gave a root mean square (RMS) surface roughness as low as 0.2 nm for the best samples, while for milky samples the surface roughness increased up to 20 nm. We suppose that the

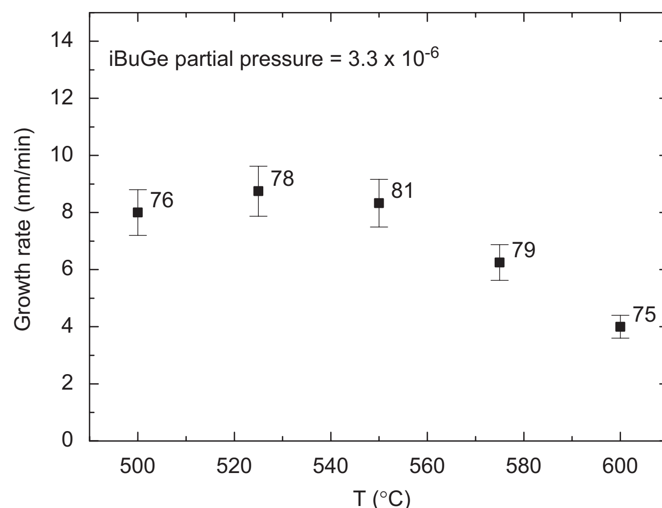

Fig. 1. Growth rate of Ge layers as a function of temperature for iBuGe partial pressure = 3.3×10^{-6} bar as measured on selectively etched GaAs substrate.

roughening process is related to the growth rate by some surface kinetic or energetic processes, as suggested by other works on Ge/Ge using GeH_4 [1–5] or by MBE [19].

Fig. 2 shows the HR-XRD results of homoepitaxial layers grown on the two types of Ge substrate with iBuGe partial pressure of 9×10^{-7} bar at 550 °C. Samples thickness was about 100 nm and the diffraction profiles of the two Ge substrates are reported as reference. A good homoepitaxial Ge/Ge structure should give an X-ray diffraction profile coincident with that of the Ge substrate, that can be considered as a perfect crystal. The broadening of the diffraction profile is thus an indication of an imperfect crystallographic quality or of the presence of a disturbed interface between substrate and epilayer.

In Fig. 2 a FWHM of 21 arcsec is obtained from the Ge/Ge epilayer grown on the (0 0 1) oriented substrate, comparable to the value of 14.5 arcsec from the Ge substrate and coincident with value expected in a perfect crystal, while a degradation of the crystal lattice is observed when the 6° off substrate is used. This behaviour was also confirmed by means of AFM analysis. Fig. 3 compares two films deposited on Ge in the same run on the exactly oriented substrate (A) and on misoriented substrate (B): the former showed a very smooth surface with some holes and an RMS surface roughness of 0.2 nm, while the latter exhibited a wave-like surface, larger pit density and ridges which resulted in an RMS roughness of 5 nm. This behaviour suggests different nucleation and growth mechanisms on the two substrates, and a specific role of the lattice steps on the growth itself. It is interesting to note that in the growth of homoepitaxial layers the substrates of choice are usually misoriented, in order to suppress island formation and to promote a step-flow growth mode. Since we get the better results with the exactly (0 0 1) oriented substrates, in the case of Ge growth with the use of iBuGe there could be other factors to consider, related for example to the surface energy or to the chemistry of the adsorbed species or to some step bunching related phenomena.

Fig. 4 shows the SEM picture of a sample grown on exactly oriented (0 0 1) substrate at 550 °C with the lowest iBuGe partial pressure employed (9.02×10^{-7} bar). Several samples with the same thickness (about 100 nm) were grown using different iBuGe partial pressures, by appropriately adjusting the growth time. Surface images were acquired both by SEM and AFM and showed similar results: the hole density decreases with the increase of the growth rate, from about $3\times10^9/cm^2$ for the sample shown in Fig. 4 to less than $4\times10^6/cm^2$ when an iBuGe partial pressure of 3.3×10^{-6} bar is used (the AFM image of this sample is given in Fig. 3B). These pits seem to have the same appearance both on the exactly oriented (0 0 1) and on the 6° off Ge substrate, so it seems difficult to state that the substrate orientation is the principal cause of the holes. TEM analysis were performed on a Ge layer grown on exactly oriented (0 0 1) substrate at 550 °C with iBuGe partial pressure of 9×10^{-7} bar. Fig. 5 is the cross section image of the sample showing a sharp layer/substrate interface, a flat surface and a hole similar to those observed by AFM. From the images obtained it appears that the pits have $<111>$ facets, do not start at substrate interface and there are no other crystallographic defects related to them.

There seems to be also a dependence of the pit density on the temperature: on samples grown at 500 °C with the same iBuGe partial pressure as the one shown in Fig. 3a the AFM analysis on a 5 μm × 5 μm area did not exhibit any hole. Further investigations are needed to understand more precisely this phenomenon. Since iBuGe decomposes at 350 °C it will be interesting to perform depositions at temperatures even lower than 500 °C, to find out if there are further improvements in the morphology without degrading the overall crystallographic properties.

Vacancy related defect in Czochralski Ge bulk wafer are a common problem. Molecular dynamics simulation showed that vacancies have the tendency to migrate and to coalesce, forming pits on the surface [20]. A similar mechanism could explain the presence of the pits observed in our epitaxial germanium, although more investigations are needed to improve our understanding.

Raman measurements on samples grown on different substrates in the same run at 550 °C with iBuGe partial pressure of 3.3×10^{-6} bar are given in Fig. 6. The acquisition time was the same for all the samples (60 s). Standard fittings performed with a mixed Gaussian–Lorentzian function reported a constant peak position of 301 cm^{-1}, while the peak FWHM is 3.2 cm^{-1} for the Ge substrate, 3.4 cm^{-1} for the sample grown on exactly oriented (0 0 1) Ge substrate, 3.5 cm^{-1} for the Ge/GaAs and 3.8 cm^{-1} for the sample grown on 6° off Ge substrate. Given the apparatus spectral resolution of 2 cm^{-1}, we should consider that all the Raman signal for all the samples are practically identical, and that the vibrational properties of the epitaxial samples are comparable to the bulk ones.

A 400 nm thick Ge layer, deposited at 550 °C with iBuGe partial pressure of 3.3×10^{-6} bar on an exactly oriented (0 0 1) p-type Ge substrate was used for preliminary electrical characterisation.

The realisation of an epitaxial p–n junction is the first step towards the achievement of a fully epitaxial TJ solar cell, avoiding the diffusion process for the doping of the bottom cell and thus is of a great technological interest.

Fig. 7 shows the typical *I–V* characteristics of a Ge-layer/p-Ge-substrate mesa structure: the junction shows a rectification ratio higher than 10^5 at 0.6 V, a reverse current density of about $2–4\times10^{-5}$ A/cm^2 and an ideality factor of 1.008–1.010. Considering the ohmicity of Au contacts and that the substrate is p-type, the good rectifying properties indicate that the nominally undoped Ge layer is n-type.

The junction has been investigated also by *C–V* measurements. It is well known that the capacitance versus voltage technique gives information about the free carrier concentration profile of the less doped side of asymmetric p+/n or (n+/p) junctions. In the present case the *C–V* measurements exhibit a flat free carrier concentration profile of about 2×10^{16} cm^{-3} up to a depth of 600 nm. Considering that: (i) the obtained carrier concentration is very near to the value given by the supplier for the p-Ge substrate and (ii) the investigated depth profile is larger than the epilayer

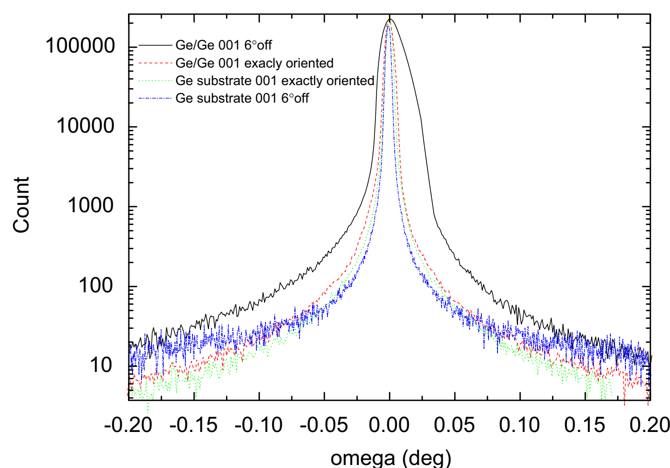

Fig. 2. XRD diffraction profiles of 2 Ge substrates (exactly (0 0 1) oriented and miscut 6° off) reported as references and of two epitaxial films grown on the same substrates at 550 °C with iBuGe partial pressure of 3.3×10^{-6} bar.

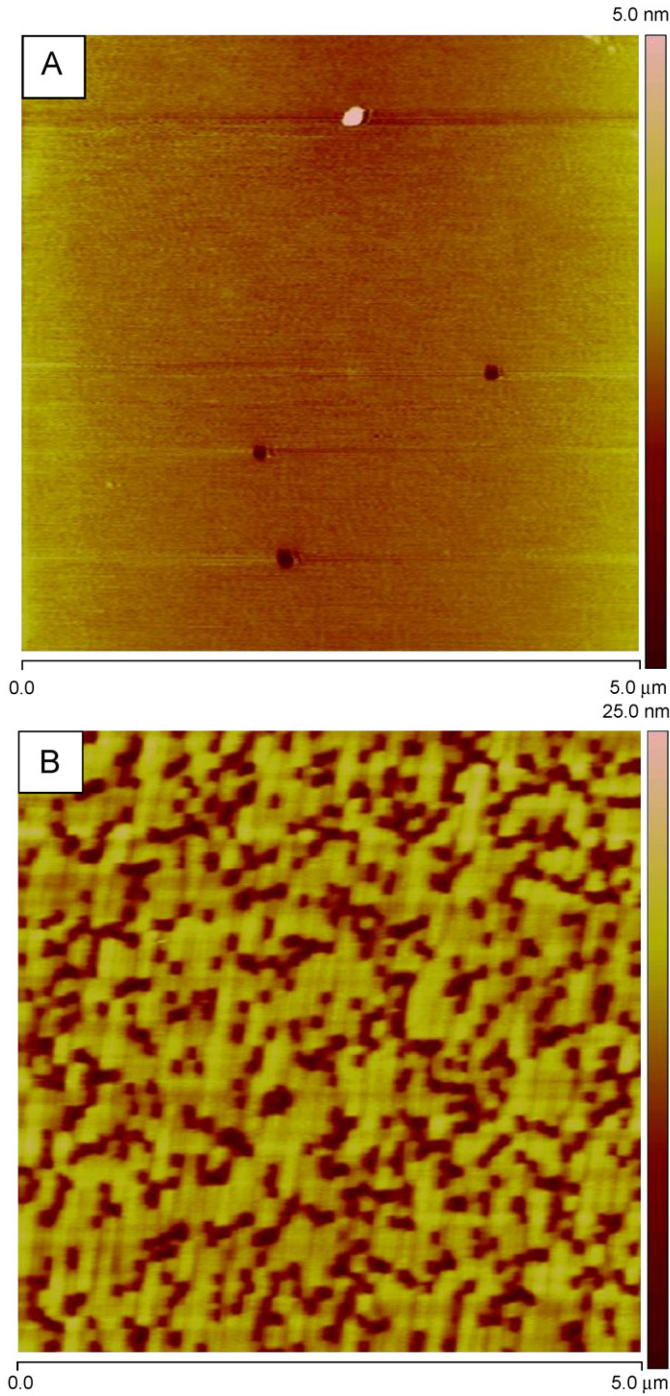

Fig. 3. AFM image of Ge epilayers grown at 550 °C with iBuGe partial pressure of 3.3×10^{-6} bar on: (A) exactly oriented (0 0 1) Ge substrate and (B) 6°off Ge substrate.

thickness, we suggest that the observed profile is related to the p-substrate and, consequently, the n-type doping of the epilayer is much higher than the doping of the p-Ge substrate.

The epitaxial n/p junction, when illuminated with a 60 W lamp, shows a clear photovoltaic effect with an open circuit voltage of about 130 mV. This epitaxial Ge cell uses the substrate as the base and an epitaxial layer as the emitter, and even if it lacks advanced post-growth process for maximising photon collection and minimising the non-radiative carrier recombination, it shows performances comparable with the one reported in literature [21].

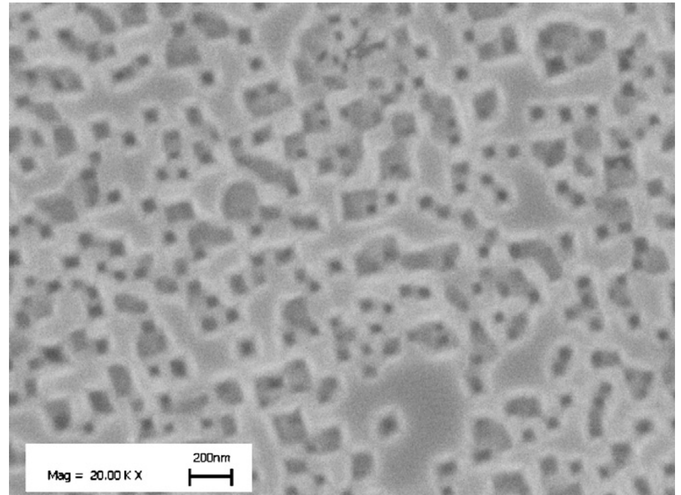

Fig. 4. SEM image evidencing pits on the surface of a sample grown at 550 °C on exactly oriented (0 0 1) Ge substrate for iBuGe partial pressure of 9.02×10^{-7} bar.

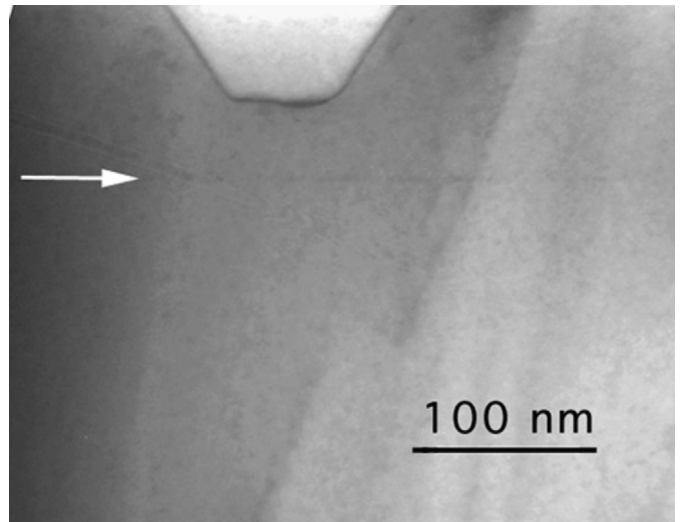

Fig. 5. Typical TEM cross section micrograph of the sample grown at 550 °C with iBuGe partial pressure of 3.3×10^{-6} bar. White arrow indicates position of the interface (weakly detectable).

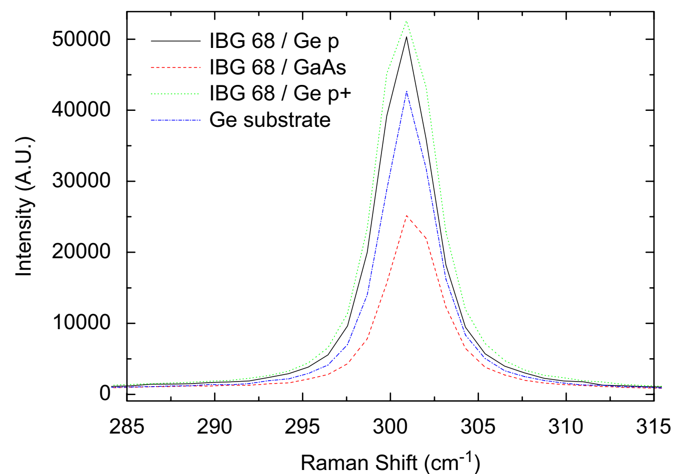

Fig. 6. Raman spectra of Ge samples grown in the same run on different substrates. The Ge substrate spectrum is shown as a reference.

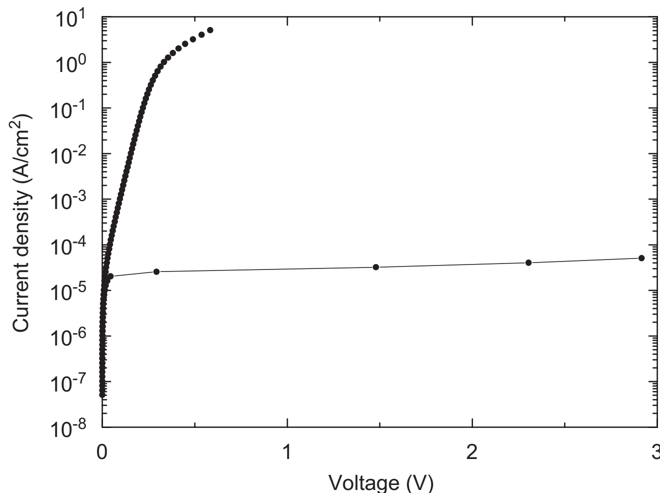

Fig. 7. *I–V* direct and reverse characteristics taken at 300 K of a mesa structure (500 μm in diameter) realised on a 400 nm thick Ge layer grown at 550 °C with iBuGe partial pressure of 3.3×10^{-6} bar.

4. Conclusions

n-Type Ge layers were epitaxially deposited on Ge substrates using only iBuGe as metal-organic precursor. A detailed study was performed on samples grown at 550 °C: the layers showed good morphological, surface and crystallographic properties when the iBuGe partial pressure was below 4×10^{-6} bar. The presence of holes on the surface was observed by both AFM and TEM and their density related to the growth rate.

Better results in terms of surface morphology and XRD peak FWHM were obtained on exactly oriented (0 0 1) Ge substrates. A good Ge/Ge interface with a low defect density was detected by TEM. Mesa structures of the Ge-layer/p-Ge-substrate samples showed very good *I–V* characteristics with rectification ratios of the order of 10^5–10^6 and ideality factor very close to unity.

Further research will be addressed to understand the origin of the pits, to minimise their appearance and to obtain a better doping control (both n- and p-type). Several basic phenomena of MOVPE growth of germanium with iBuGe still need an in-depth study, as the influence of the substrate orientation on the crystallographic properties and the growth rate drop at higher temperature.

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