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Low Temperature Selective Growth of Ga-Doped and Ga-B Co-Doped Germanium Source / Drain for PMOS Devices

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Abstract

The peculiarities and physical properties of gallium-doped (Ge:Ga) and gallium and boron co-doped germanium (Ge:Ga:B) epilayers grown at low temperature (320°C) by chemical vapor deposition are investigated and benchmarked against their boron-doped (Ge:B) counterpart. Ge:Ga films with resistivities < 0.3 mΩ cm are demonstrated, outperforming Ge:B prepared with a similar method. A selective Ge:Ga growth process based on a cyclic deposition and etch routine is developed and applied to fin structures. Full process selectivity towards nitride and oxide surfaces is demonstrated. Ga incorporation is however reduced, compared to non-selective growth, resulting in a degradation of the electrical performance. Ti / Ge:Ga(B) contacts are finally evaluated, with the aim of providing new solutions for advanced Ge-based devices.

1. Introduction

Achieving very high doping concentrations in group-IV semiconductor materials is of prime importance for the next generations of metal-oxide-semiconductor field-effect transistors (MOSFET). This allows to decrease the contributions from parasitic contact resistances to the devices, which limit the performance at scaled dimensions.1 Significant efforts have been devoted to maximizing the active doping concentrations in e.g. n-Si, p-SiGe, and Ge with free hole densities up to ~ 1.6x10^20 cm^-3 (resistivity ~ 0.5 mΩ cm) in Ge_0.95Si0.05.2-4 and in Ge_0.9Sn0.05.5-7 Although the material quality was degraded above those concentrations, low ρc values in the low 1x10^-9 Ω cm^-2 regime could be demonstrated.

Huffinan and Casey initiated the chemical vapor deposition (CVD) assessment of Ge:Ga by flowing GeCl4 and GaCl3 as Ge and Ga precursors, respectively.8 However, the choice of the GeCl4 precursor was motivated by former works done on the Si:Ga system,9 where the halide precursor prevented risks for unwanted C incorporation.10 Although the C solubility in Ge is extremely low,11 The method resulted in films with high purity. However, in the range of explored conditions, only low doping levels ([Ga] ≤ 1x10^17 cm^-3) could be obtained, likely due to the low vapour pressure of the solid GaCl3 precursor.

Metalorganic (MO) precursors constituted a credible alternative for enabling higher doping levels thanks to higher partial pressures. Considering safer precursors, Jakomin et al. proposed the use of the unconventional iso-butyl germane precursor in combination with trimethylgallium (TMGa). Thick Ge:Ga films could then be grown at 550 and 670°C with free hole densities up to ~ 2x10^21 cm^-3.12 However, defects related to the formation of Ga droplets during deposition were observed when exceeding a concentration of ~ 1x10^19 cm^-3. Two options were proposed and validated to avoid the formation and coalescence of Ga-rich clusters: operate at relatively high temperature (670°C), at which superficial Ga in excess can desorb rapidly, or work with limited Ga precursor flows and reduced thermal budgets (550°C), where the importance of diffusion phenomena is reduced. Jin et al. confirmed this statement by suppressing the occurrence of Ga clustering during the epitaxy Ge:Ga on GaAs using germane (GeH2) and TMGa thanks to an increase in growth temperature.13 Finally, Xu et al. broke the 2x10^20 cm^-3 active concentration wall in defect-free Ge:Ga by taking advantage of
CVD reactions between tetragermane (Ge2H6) and dimethylamine-gallane ([D2GaN(CH3)2]3). The reaction yielded epitaxial films with nearly full doping activation up to 2.7x10^20 cm^-3 (resistivity ~ 0.4 mΩcm) at temperatures as low as 360°C, undeniably providing a step forward in the quest for highly doped Ge:Ga. However, the proposed precursors are not standardly available and the method is, at the moment, not scalable to large production.

In this manuscript, commercial precursors are instead considered, following preliminary works done on the SiGe-B:Ga material system with other precursors. The work was introduced in an extended SSDM abstract and takes advantage of the cyclic deposition-etch (CDE) method previously described in the case of Ge:B epilayers to develop selective growth conditions for Ge:B. With respect to the previous report, additional background information regarding the Ga precursor selection and experimental conditions are provided. The physical properties of Ge:Ga layers deposited with standard and selective growth conditions are discussed in more detail. The resulting Ga chemical concentration profiles are e.g. compared, which allows to identify some limitations of the proposed process. Early results from Ga-B co-doping are also presented.

First, the physical properties of the grown Ge:Ga materials are evaluated. Selective epitaxial growth (SEG) conditions are demonstrated on Ge fins with SiNx spacers. Next, the limitations associated to the SEG process performance are discussed. Finally, the co-doping with Ga and B is addressed as a potential way to further boost the material electrical properties. A first assessment of Ti / Ge:Ga:B contact properties is proposed, using the multi-ring circular transmission line method (MR-CTLM) introduced earlier. This study constitutes a first evaluation of the new possibilities offered by Ga doping for the performance improvement of Ge-based devices.

### Table 1. Characteristics of several Ga precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Chemical Formula</th>
<th>Molecular mass (g/mol)</th>
<th>Vapor pressure at 20°C (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethyl-gallium (TMGa)</td>
<td>Ga(CH3)3</td>
<td>114.8</td>
<td>~ 180</td>
</tr>
<tr>
<td>Triethyl-gallium (TEGa)</td>
<td>Ga(C2H5)2</td>
<td>156.9</td>
<td>~ 5</td>
</tr>
<tr>
<td>Tri-tertiary-butyl-Gallium (TTBGa)</td>
<td>Ga(C(CH3)2)3</td>
<td>241.1</td>
<td>~ 1</td>
</tr>
<tr>
<td>Gallium trichloride</td>
<td>GaCl3</td>
<td>176.1</td>
<td>~ 0.1</td>
</tr>
</tbody>
</table>

The growth experiments were performed on 600 nm thick mildly As-doped (~ 1x10^17 cm^-3) Ge virtual substrates (VS) at reduced pressure and a setpoint temperature of 320°C (Fig. 1(a)). It may be important to note that this nominal temperature was measured by thermocouples positioned on the backside of the susceptor holding the wafer and may be lower than the actual surface temperature. Low temperature processing was preferred in view of maximizing Ga incorporation while preventing its segregation. As the considered low temperature epitaxy process is non-selective, it was combined with a selective etching using Cl2 in a reproducible isothermal and isobaric CDE routine. Tuning the deposition and etch durations allowed to setup conditions avoiding the deposition of polycrystalline Ge grains on Si oxide and nitride surfaces present on wafers patterned with Ge fins (Fig. 1(b) and Fig. 2).

![Fig. 1. Schematics describing the growth experiments performed on (a) Ge:As virtual substrates and (b) wafers patterned with Ge fins, including 80 x 80 µm² measurement pads and areas with fins of different dimensions.](image)

Adjusting the number of CDE cycles allowed to obtain the desired material thickness. The grown epi materials were characterized by differential mass measurements and X-ray reflectivity (for thickness extraction), top view scanning electron microscopy (SEM, for morphology evaluation), secondary ion mass spectrometry (SIMS, for compositional analysis), micro-4-point-probe and micro-Hall effect (MHE) measurements (for electrical assessment).
rate (GR) of ~ 7.9 nm/min. It exhibits a smooth surface and a resistivity $\rho_{Ge:Ga}$ of 0.55 m$\Omega$ cm. The active doping concentration ([Ga]$_{act}$), estimated from MHE assuming a Hall scattering factor (HSF) of 1, amounts to 1.9x10$^{20}$ cm$^{-3}$. The extracted Hall carrier mobility is $\mu_H = 61$ cm$^2$.V$^{-1}$.s$^{-1}$. The estimated [Ga]$_{act}$ exceeds the chemical Ga concentration ([Ga]$_{chem}$) of 1.4x10$^{20}$ cm$^{-3}$ extracted by SIMS. A best assumption therefore is that most of the Ga dopants present in the sample are electrically active. This is supported by X-ray absorption fine structure measurements, performed on similar samples and combined with density functional theory analysis, reported in [32]. Those indeed indicated that the majority of the Ga impurities were occupying substitutional sites in the Ge matrix. A full activation of the dopants can however not be confirmed due to a lack of literature reports on HSF values for high doping levels. This result nevertheless suggests that the HSF cannot be larger than 0.74, as the electrically active doping concentration cannot exceed the chemical doping concentration.

As expected, [Ga]$_{chem}$ and [Ga]$_{act}$ increase with increasing the TTBGa precursor flow. Sample B (Fig. 3(b)), grown with TTBGa flow $F_2 = 2.5$ a.u., is a bit thinner and has a resistivity as low as 0.28 m$\Omega$ cm. [Ga]$_{chem}$ amounts to 3.6x10$^{20}$ cm$^{-3}$, one of the highest doping levels reported so far. For this sample, the HSF is necessarily $\leq 0.55$, with [Ga]$_{act} = 6.6x10^{20}$ cm$^{-3}$ and $\mu_H = 33$ cm$^2$.V$^{-1}$.s$^{-1}$. The observed decrease in Hall mobility, dominated by Coulomb scattering, supports an increase in active doping.

Beyond TTBGa flow $F_2$, Ga clustering cannot be prevented. Sample C (Fig. 3(c)), grown with TTBGa flow $F_3 = 5$ a.u., exhibits surface defects identified as Ga-rich clusters. A critical TTBGa partial pressure for cluster formation in these growth conditions is therefore determined. Saturations in $\rho_{Ge:Ga}$, [Ga]$_{chem}$, [Ga]$_{act}$, and $\mu_H$ are observed.

4. Selective Ge:Ga growth on fins

Cl$_2$ etching steps were introduced in the deposition process and the resulting CDE routine applied to Ge fins with nitride spacers and separated by SiO$_2$ shallow trench isolation to confirm process selectivity (Fig. 1(b)). Net growths per cycle of ~ 3 and 3.5 nm were obtained on blanket Ge and pads present on fin wafers, respectively (Fig. 4). As observed on samples A, B and C (epi only), the growth rate on blanket
wafers decreases with increasing the TTBGa flow. The trend is modified on fin wafers, where the net growth per cycle is enhanced due to loading effects. Moreover, for the given process conditions, it remains approximately constant until a critical TTBGa flow of ~4 a.u. is reached. It then decreases sharply, indicating a faster etching rate on materials with higher doping.

Fig. 4. Growth per cycle as a function of TTBGa flow for CDE processes applied to blanket Ge (red triangles) and fin wafers (black squares).

Fig. 5 presents SEM inspection results after Ge:Ga SEG on Ge fins. Two different CDE recipes, with low (4 a.u., Fig. 5(a-b)) and high (10 a.u., Fig. 5(c-d)) TTBGa flows, result in SEG towards the oxide and nitride surfaces present on the test wafers. The materials grown with the low TTBGa flow exhibit smooth surfaces on both wide (Fig. 5(a)) and narrow (Fig. 5(b)) fins. However, exceeding the critical TTBGa precursor flow causes a roughening of the Ge:Ga films deposited on metrology pads (not shown here). Such conditions also prevent Ge:Ga from growing on narrow fins (Fig. 5(d)). The proximity of nitride and oxide surfaces indeed induces material faceting at the sidewall interface\cite{33}, which causes stress and enhanced epi defectivity on slow-growing \{111\} or \{113\} crystallographic planes.\cite{34}

The CDE routine also affects the electrical properties. Fig. 6 shows the evolution of material resistivity as a function of TTBGa flow for Ge:Ga layers grown without and with the CDE process. For a given TTBGa flow, implementing the CDE results in a significant increase in resistivity. This is explained by a reduced Ga incorporation, as confirmed by SIMS in Fig. 7.

For a Ge:Ga layer grown with a TTBGa flow of 4 a.u., employing the CDE routine suppresses up to ~85% of the incorporated Ga, likely consumed under the form of GaCl₃ by-products during growth. [Ga]_{chem} ~ 7x10^{19} cm⁻³ remain present in the film. MHE measurements do not indicate any deactivation of these residual Ga dopants. Solutions clearly need to be identified to restore Ga incorporation up to competitive levels. Using higher TTBGa flows to compensate for the loss allows to incorporate up to [Ga]_{chem} ~ 1.5x10^{20} cm⁻³ using CDE (not shown here). This is however not an option in view of growth on patterned structures, since higher TTBGa flows lead to low growth rates and even no deposition on narrow fins, as seen in Fig. 5. Extending the Cl₂ purging time between two consecutive etch and deposition steps may nevertheless enhance the achievable Ga doping levels by limiting interactions between Ga and Cl species.

The CDE routine also affects the electrical properties. Fig. 6 shows the evolution of material resistivity as a function of TTBGa flow for Ge:Ga layers grown without and with the CDE process. For a given TTBGa flow, implementing the CDE results in a significant increase in resistivity. This is explained by a reduced Ga incorporation, as confirmed by SIMS in Fig. 7.

Fig. 6. Ge:Ga bulk resistivity as a function of TTBGa flow used during growth, in the case of blanket epitaxy without Cl₂ (blue circles), blanket epitaxial growth with Cl₂ etching steps (red triangles) and the CDE procedure applied to fin wafers (black squares).

Fig. 7. Chemical Ga concentration profiles extracted from 2 Ge:Ga grown with a TTBGa flow of 4 a.u., without (blue dots) and with (red triangles) the CDE routine.
5. Ga-B co-doping in Ge

Another approach consists in co-doping the Ge layer with Ga and B. Combining two dopants may enable higher active doping concentrations, thanks to strain compensation effects and/or by limiting doping deactivation by, e.g., suppressing free vacancies in the host matrix. A preliminary assessment of the non-selective growth of Ge:Ga:B was therefore conducted.

A reference Ge:B epilayer resulting being ~ 88 nm thick with a resistivity ~ 0.55 mΩ·cm. [B]act, estimated using MHE assuming HSF = 1, yielded ~ 1.1x10^20 cm^-3 (μH = 102 cm²·V^-1·s^-1). Ga was then introduced to grow Ge:Ga:B in similar conditions (all other parameters kept same). The layer was then slightly thinner, ~ 83 nm thick, with a similar apparent resistivity ~ 0.54 mΩ·cm. [Ga+B]act was estimated ~ 1.4x10^20 cm^-3 (μH = 78 cm²·V^-1·s^-1). No morphology degradation was observed.

SIMS measurements were performed to access the B and Ga concentration profiles throughout the layers. Results are presented in Fig. 8. The Ge:B epilayer features a box-like B doping profile with a flat B level of [B]chem = 4x10^19 cm^-3. The Ge:Ga:B layer, however, features a different B profile, with a monotonic decrease from [B]chem = 4x10^20 down to 6x10^19 cm^-3 towards the sample surface. This phenomenon is assumed to be due to competitive reactions for B and Ga incorporation at the surface of the sample during growth. In the first few nm, B incorporates normally and reaches the same level as in the Ge:B sample. Ga incorporation is delayed and takes off after a Ge thickness of 5-7 nm. As discussed in previous studies, Ga indeed first accumulates at the sample surface before it starts incorporating in the growing layer. The surface is then partly occupied, which apparently decreases the B incorporation efficiency. Consequently, the Ga signal increases towards the surface to saturate around [Ga]chem = 9x10^19 cm^-3, while B incorporation reduces significantly. The activation level [Ga+B]act/[Ga+B]chem could be estimated by integrating the total dopant dose in the sample, and resulting close to 60%.

These results however suffer from significant error bars (due to the non-ideal profiles in Ge:Ga:B and HSF values which can differ for B and Ga dopants) which prevent from drawing conclusions on a possible increase in hole active doping concentration in p-doped Ge thanks to co-doping. Additional investigations are needed to clarify this point. Moreover, the impact of Ga-doping on the resulting B concentration profile suggests the occurrence of complex interactions between the dopant adatoms and/or precursors during surface reactions. These learnings will be leveraged for the design of future studies and process developments.

6. Ti / Ge:Ga:B contact resistivity assessments

The specific resistivity (ρc) of metal to S/D contacts is an important metric characterizing their performance. Some of the developed materials were therefore used for blanket contact studies.

ρc values down to 3.1x10^-6 Ω·cm² were e.g. extracted from Ti / Ge:Ga contacts based on non-optimized Ge:Ga epilayers with bulk resistivity down to 0.55 mΩ·cm. Similar tests were conducted with Ti / Ge:Ga:B and confirmed cumulative effects from moderate (~ 8 x10^19 cm^-3) Ga-B co-doping in comparison to samples with one single dopant. For instance, Ti contacts formed on Ge:Ga (~ 1x10^19 cm^-3, ρGe:Ga = 2.10 mΩ·cm) grown with TTBGa flow F_{Ga} and Ge:B ([B]_act ~ 6x10^19 cm^-3, ρGe:B = 0.80 mΩ·cm) grown with B_{2}H_{6} flow F_{B}, yielded ρc ~ 4.8x10^-6 Ω·cm². Corresponding contacts to non-optimized Ge:Ga:B (ρGe:Ga:B:act = 0.49 mΩ·cm) grown with TTBGa and B_{2}H_{6} flows F_{Ga} and F_{B}, yielded ρc ~ 4.8x10^-6 Ω·cm². Further investigations in the high doping regime are required to assess the ultimate contact resistivity scaling achievable with this method.

In the end, the reported Ti / Ge:Ga:B contacts do not outperform Ti / Ge:B stacks (ρc < 3x10^-6 Ω·cm² in this new study) down to ~ 2x10^-6 Ω·cm² in this new study). Nevertheless, the extracted contact resistivities enter the low 1x10^-9 Ω·cm² regime, which demonstrates some potential for Ga-doping in Ge in view of S/D applications in Ge-based devices.

7. Conclusions

This paper summarizes the development of low temperature, highly doped and selectively grown Ge:Ga source / drain materials, using a cyclic routine compatible with advanced device geometries. Ge:Ga films with box-shaped doping profiles and bulk resistivities < 0.3 mΩ·cm are achieved, which outperforms the best Ge:B materials prepared with a similar method. Although the specific resistivity of Ti / Ge:Ga contacts is not yet as low as that of Ti / Ge:B stacks, epi materials...
presented in this work remain attractive for Ge PMOS devices. The main challenge ahead is to overcome the limitations linked to the selective implementation of the developed materials. Solutions based on Ga-B co-doping may have potential to overcome these difficulties.

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