

Low temperature *in-situ* P-doped Ge epitaxy using Ge₂H₆ in view of optical applications

Yosuke Shimura,^{1,2} Ashwyn Srinivasan^{1,3,4}, Dries Van Thourhout^{3,4}, Rik Van Deun⁵,
Marianna Pantouvaki¹, Joris Van Campenhout¹, Roger Loo¹

¹ imec, Leuven, Belgium, ² Instituut voor Kern- en Stralingsfysica, KU Leuven, Leuven, Belgium, ³ Photonics Research Group (INTEC), Ghent University-IMEC, Ghent, Belgium, ⁴ Center for Nano- and Biophotonics (NB-Photonics), Ghent University, Ghent, Belgium, ⁵ L³ – Luminescent Lanthanide Lab, Department of Inorganic and Physical Chemistry, Ghent University, Ghent, Belgium

*Corresponding author. E-mail address: shimura@imec.be

The availability of a highly n-type doped Ge is of key importance for a range of electrical and optical applications. A well-known example is the realization of a quasi-direct band transition by high n-type doping which fills up both the L-valley and the Γ -valley [1] which has been studied to realize Ge based lasers. The solubility limit of P in Ge increases with temperature, and eventually it reaches the maximum solubility, $7 \times 10^{19} / \text{cm}^3$ at 850°C [2]. This value is same as the required carrier concentration to achieve the quasi-direct band transition for a 0.25% tensile strained Ge. However, such a high processing temperature is not compatible with other Ge processes, such as CMOS flows. In order to obtain a higher carrier concentration than the solubility limit at low temperatures, a non-equilibrium doping process is required. Recently, *in-situ* doping during epitaxial growth at low temperature which leads non-equilibrium incorporation of the n-type dopant has been gathering attention [3,4]. We will report the impact of growth conditions (temperature, partial pressure (pp) ratio of precursor gases) on the n-type dopant incorporation. A higher order Ge precursor gas, namely Ge₂H₆ has been used, to maintain an acceptable growth rate at the reduced growth temperature.

Ge₂H₆ (1% diluted in H₂) and PH₃ (5% diluted in H₂) were used as precursor gases. A conventional 1 μm thick Ge buffer layer grown on Si(001) substrate was used as a virtual substrate [5]. The Ge buffer layer has a tensile strain of 0.16% from the thermal expansion coefficient mismatch. In this contribution we discuss *in-situ* P doped epitaxial Ge growth with a fixed Ge₂H₆ flow in H₂ ambient on top of the virtual Ge substrate using reduced pressure chemical vapor deposition (CVD). This because, during epitaxial growth at atmospheric pressure, significant P diffusion into the Ge buffer layer occurs, which was not observed if growth was performed at reduced pressure. The origin of this P diffusion is currently not understood and being investigated. The crystal quality in terms of optical applications was studied by photoluminescence (PL) at room temperature.

For relative low P concentration in the epitaxial Ge, the P is fully active (Fig. 1). For growth temperatures of 320°C and 425°C, we extracted chemical P concentrations which are close to the expected P density as calculated from the pp ratio assuming same adsorption coefficients for PH₃ and Ge₂H₆ (dashed line in Fig. 1). With increasing ppPH₃, the chemical P concentration starts to saturate, and the measured chemical P concentration deviates from the calculated value. It is noted that the maximal possible chemical P concentration increases with decreasing growth temperature. Reducing the growth temperature moves the growth process further away from the equilibrium. This explains why at high ppPH₃'s, also the active dopant concentrations are higher at 320°C than at 425°C (Fig. 2). The increase in maximal achievable carrier concentration with decreasing growth temperature is directly reflected in the PL intensity (Fig. 3) As long as the P-dopants are fully active, the PL intensity increases with the carrier concentration. The highest PL intensity is measured for the Ge layer grown at the lowest growth temperature because at this temperature the highest electron concentration is obtained. On the other hand, the PL intensity is sensitive to the density of point defects. Point defects can be caused by e.g. limited dopant activation or by epitaxial growth at extremely low growth temperatures. For layers with a high chemical P concentration, which are not fully electrically active (open symbol in Fig. 3), we measured a reduced PL intensity. The concern that a low growth temperature leads to a degraded material quality was not confirmed. PL intensities for Ge layers grown at 320°C and 550°C are comparable for comparable active P concentrations indicating that the optical material quality is similar. On the other hand, the layer quality is drastically improved by annealing. P doped Ge shows a strong increase of the PL intensity after post-epi annealing at 700°C for 30 sec in N₂ ambient (Fig. 3).

As a conclusion, lowering the growth temperature of P doped Ge epitaxial layer enables to increase the efficiency of light emitting because it enables higher dopant activation. Post epi anneals allow to increase the PL intensity even further.

References:

[1] X. Sun, *et al.*, IEEE J. Sel. Top. Quantum Electron. **16**, 124 (2010).
 [2] R. Olesinski, *et al.*, J. Phase Equilibria, **6**, 262 (1985).
 [3] J. M. Hartmann, *et al.*, J. Cryst. Growth, **347**, 37 (2012).
 [4] G. D. Dilliway, *et al.*, ECS Trans. **3 (7)**, 599 (2006).
 [5] A. Malik, *et al.*, IEEE Photonics Technology Letters, **25(18)**, 1805 (2013).

Acknowledgements:

Y. Shimura acknowledges the Research Foundation of Flanders (FWO) for granting him a fellowship within the Pegasus Marie Curie Program. D. Van Thourhout and R. Van Deun acknowledge support from the Hercules foundation (project AUGÉ/09/024 “Advanced Luminescence Setup”). We thank the financial support via the Support of Public and Industrial Research using Ion Beam Technology (SPIRIT) project (contract No. 227012) and the KU Leuven project GOA/2009/006. We also thank ASM and the imec core partners within imec’s Industrial Affiliation Program on Logic and Optical IO. Air Liquide Advanced Materials is acknowledged for providing Ge₂H₆.

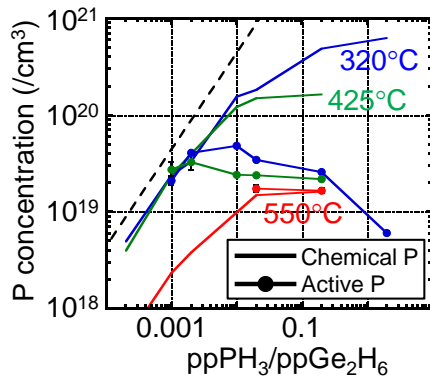


Fig. 1. Chemical and active P concentration as measured by SIMS and micro 4 point probe combined with Hall effect measurements, respectively. The dashed line is the expected P concentration calculated from the pp ratio assuming the same adsorption coefficients for PH₃ and Ge₂H₆.

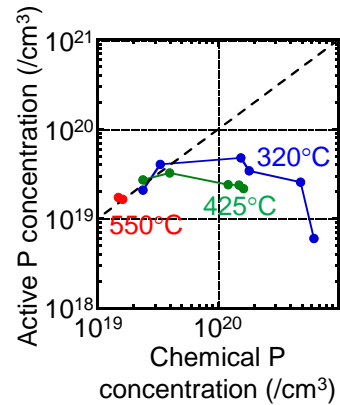


Fig. 2. The active P concentration as a function of the chemical P concentration.

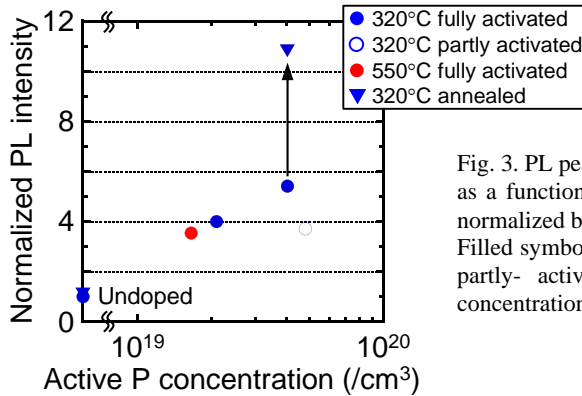


Fig. 3. PL peak intensity for as-grown and annealed Ge layers as a function of active P concentration. The PL intensity is normalized by the as-grown undoped sample grown at 320°C. Filled symbols and the open symbol correspond to fully- and partly- activated samples, respectively. The chemical P concentration of the open symbol is $1.6 \times 10^{20} / \text{cm}^3$.