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Electrical and Structural Properties of In and In + C Doped Ge

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In order to follow the downward scale trend in the semiconductor technology it is necessary to find a replacement for the current technology based on Si which is reaching its physical limits. Germanium has been considered as a promising candidate as it offers superior electron (∼ 2×) and hole (∼ 4×) mobility compared to Si. The low activation energy (0.0112 eV) and low diffusion coefficient of Indium in Ge makes it an ideal p-type dopant for Ge, which benefits both device performance and scaling [1]. Since lattice structure significantly influences electrical properties, a detailed study of the In-doped Ge lattice configuration is necessary to understand the effects of doping concentration and defect environments that ensue with processing.

In this contribution, we have used synchrotron based analytical techniques of x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure spectroscopy (EXAFS) to study the atomic-scale environment of In-doped Ge. In addition, we studied the option of co-doping Ge with its isovalent element C. In the past, In + C co-doping has been studied in Si. It has been found that In has a preference to pair with C suppressing precipitation of In and allowing for high electrically-active fractions to be achieved [2]. Intuitively, a similar effect can be expected for Ge. We then correlate the obtained structures with the observed electrical properties characterized by Hall Effect measurements. A range of complementary techniques including Rutherford Backscattering Spectrometry (RBS), Raman spectroscopy and transmission electron microscopy (TEM) were also used. Here TEM has a fundamental role in the characterization providing a link between the atomic scale information provided by the synchrotron based techniques and the electrical measurements. Finally, first principles calculations were performed in the framework of density functional theory (DFT) in order to aid the XANES and EXAFS parameter optimization.

For this, nominally undoped Ge layers of thickness 1.8 μm were grown in Si (001) substrates by ultra-high vacuum chemical vapor deposition and then implanted. The ion implantation temperature was set to 250 °C and the angle was set to 7° to avoid amorphization and channeling effects respectively. The In implantation energies and fluences were estimated in order to produce a uniform depth distributions over 0.2-1.2 μm with concentrations ranging from 0.02 to 1.3 at. % as determined by RBS. For the C co-doped group energies and fluences were then estimated in order to yield overlapping C and In depth distributions at a 1:1=In:C concentration ratio in each sample. A three step annealing in N_2 at 550, 450 and 350 °C for 0.5, 1.0 and 2.0 h respectively was then employed to reduce lattice disorder and promote the formation of In related defects by reducing its solid solubility with decreasing temperature.

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Table 1 summarizes the results obtained from the EXAFS fittings using the optimized structures obtained by DFT. The results show that for the system implanted only with In, pairing of dopants starts at concentrations bellow 0.6 at. % (63 ± 4 % In metal fraction) leading to a fraction of electrically activated In of only 21 % consistent with a lower coordination number CN_{Ge} = 3.1 ± 0.4. Further increasing the amount of In dopants only leads to an increase of the metallic fraction to 72 ± 5 without any improvement in the electrical properties. Conversely, for the co-doped system an activated fraction of 63 % was observed at 0.65 at. %. The results show that by pairing with C, In can maintain a four-fold coordinated state leading to a drastic improvement in the electrically activated fraction in relation to a similar 0.6 at. % In doped sample. In this system no sign of In metal pairing up to 1.3 at. % (Table 1) was observed. However, at the highest In concentration no electrical improvement was observed due to an increased number of scattering centers consistent with the higher level of disorder described by the DWF (Table 1). The TEM demonstrates that the arising of an In metal fraction can be correlated to the formation of In nanoparticles for concentrations as low as 0.6 %. Further increasing the atomic concentration only leads to the formation of larger In particles with a cuboctahedron shape. Finally, it is important to note that even for the highest implantation fluence no In related nanoparticles were observed in the In + C doped system [3, 4].

In conclusion, we have characterized the electrical and structural properties of In implanted and In + C implanted Ge. We demonstrate that the co-doping process leads to the suppression of metal-metal pairing allowing In to maintain its four-fold coordinated electrically activated structure in Ge resulting in much improved electrical properties. Therefore this work demonstrates that the co-doping of In with isovalent elements is an effective strategy high electrically activated dopant fractions required for advanced devices. [5]

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In (and C) concentration (at. %)	In metal fraction (%)	CN_{Ge} (atoms)	CN_C (atoms)	DWF (x10^{-3} Å^2)
In doped Ge				
0.02	0	4	~	3.2, 4.1, 6.4
0.06	0	4	~	3.4, 4.6, 7.1
0.2	0	4	~	3.6, 5.1, 7.4
0.6	63 ± 4	3.1 ± 0.4	~	3.6, 5.5, 7.1
1.2	72 ± 5	2.6 ± 0.5	~	3.9, 5.6, 6.8
C + In doped Ge				
0.07	0	4	0	3.3, 4.2, 6.7
0.2	0	3.65 ± 0.17	0.35 ± 0.17	3.5, 4.9, 7.3
0.65	0	3.45 ± 0.11	0.55 ± 0.11	3.8, 5.5, 7.7
1.3	0	2.71 ± 0.11	1.29 ± 0.11	4.2, 6.3, 9.4

Table 1: The In metal fraction, coordination numbers of the first nearest neighbor Ge and C to In, (CN_{Ge} and CN_C, respectively) and Debye-Waller factors (DWF) of the first, second and third Ge shells for In doped Ge and C + In doped Ge samples. Reprinted with permission from Appl. Phys. Lett. **107**, 212101 (2015), Copyright 2015 AIP Publishing LLC.

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